# DISPOSAL OF OILFIELD WASTES BY LAND TREATMENT IN ALBERTA: SUMMARY REPORT ON FEASIBILITY, ENVIRONMENTAL RISK ASSESSMENTS AND FUTURE LAND USE

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A report prepared for:
The Canadian Petroleum Association
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CANADIAN PETROLEUM ASSOCIATION

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## EXECUTIVE SUMMARY

A program was initiated in 1982 and concluded in 1989 to determine the feasibility of using the land treatment/biodegradation method for the disposal of select oil field production facility wastes in Alberta. Emphasis was placed on determining rates of degradation of hydrocarbon wastes under different soil and climatic conditions, methods to enhance biodegradation, effects on surface and groundwaters, uptake of organic compounds by plants, and reclamation of land treatment sites.

Demonstration plots were established at the following Alberta locations: Lloydminster; Grande Prairie; Drayton Valley; and Brooks. Oily wastes were applied once per year for two to four years at these sites. At Lloydminster heavy oil wastes such as tank bottoms and slop oil were applied and at the other three sites untreatable residuals from reclaiming plants were used for land treatment. Four levels of sludges were applied at each site but amounts added varied among sites and between years depending upon materials available and the desired adjustments of oil levels in the soil. At each site two levels of fertilization and two frequencies of cultivation were also included as treatments. All plots were limed to above pH 7 to reduce the leaching of heavy metals. Soil oil (hydrocarbon) contents, soil inorganic chemistry and groundwater and surface water quality were monitored periodically at all sites. After oily waste applications had ceased, all sites were planted to field crops and plant yield measured. Detailed assessments of crop production, groundwater quality, crop quality and reclamation procedures were conducted at the Lloydminster site.

None of the parameters measured, including oil degradation rates, appeared to be influenced by either cultivation frequency or fertilization rates. Both of these factors may influence oil degradation rates but either both rates used were in the optimum range or, more probably, variability under field conditions precluded the detection of treatment effects.

The oil contents of the soils ranged from 0.8 to 13.5% over the course of the study, but were generally maintained between 3 and 6% and degradation occurred relatively rapidly at all oil concentrations. It was assumed that microbial decomposition was the major agent responsible for the disappearance of hydrocarbons although it was recognized that volatilization of low molecular weight compounds occurred, especially immediately after sludge applications. During the first year, 70% of the oil disappeared at the Grande Prairie site, 50% at Drayton Valley, 23% at Brooks, and 14% at Lloydminster. The large differences in decomposition (plus volatilization and nonbiological degradation) rates may have been due, at least in part, to the heavier nature of the oil at the latter two sites. Additional oil applications were made to all sites except Brooks and after yearly applications were made for 3 years, 71% (130,000 kg $ha^{-1}$) of oil had degraded at Grande Prairie, 71% (216,000 kg $ha^{-1}$) at Drayton Valley, and 49% (179,000 kg $ha^{-1}$) at Lloydminster. It appeared that the loading potentials of the soils were very high as similar rates of degradation could be found with soil oil contents as high as 13.5%. Only at Lloydminster, where the least rapidly degraded oil was applied, were the studies continued for the full 8 years and at the end of that period, 4 years after the last application of oil, 73% (196,000 kg $ha^{-1}$) of the oil had degraded. In the final 3 years of the study, the average amounts of degradation (all treatments combined) were 15, 23 and 10% with a final soil oil content of 3.1%. Only in the last year did degradation rates diminish substantially.

Despite expectations to the contrary, there was not an accumulation of asphaltenes in the soil at Lloydminster but rather a steady decrease after the final oil application was made; specifically, asphaltenes in the soil decreased 14, 15 and 17% in each of the last 3 years. The asphaltene content of the oil ranged from 19 to 23% in the same period with no obvious increase in heavy oil fraction with time.

The oil was non-mobile at all four sites with only traces being detected below the cultivation zone (0-30 cm). Four years after the last application of oil a search was made in the upper 45 cm soil

at Lloydminster for low molecular weight aromatic compounds which could represent future groundwater contaminants. None of the eight target compounds (dibenzothiophene, pyridine, carbazole, 2-methyl naphthalene, biphenyl, acridine, 4-methyl biphenol and 9-ethyl fluorene) were detected in the soil at any depth.

The soil reaction remained above pH 7 for the entirety of the study at all four sites and thus the chance for heavy metal leaching was low. The addition of oil sludges to soils resulted in increased sodium adsorption ratios and electrical conductivities and increased concen- trations of chlorides, sodium and sulphates. Despite yearly applica- tions of fertilizer, levels of inorganic nitrogen were very low in the soils treated with oily sludges.

At three sites, Grande Prairie, Drayton Valley and Brooks, hay or dryland pasture species were planted 2 years after the last oily sludge application. Growth of alfalfa and timothy at Grande Prairie was poor in the final year but improved marginally in the second growing season. At Drayton Valley growth of timothy and red fescue in the first year ranged from good to poor, with good growth occurring on plots with soil oil contents below 2.5% and poor growth occurring when oil contents exceeded 3.5%. Soil inorganic chemistry on plots where growth was good did not differ from that of untreated soil. The establishment of dryland pasture species at the Brooks site appeared to be restricted by a combination of oil stress and microenvironmental moisture conditions although good growth occurred in the second year on soil with relatively low oil contents.

A more detailed study of the relationship between plant growth and soil oil content was made at Lloydminster where barley was grown for four successive years and standard agricultural practices were used to rehabilitate the soil. When the first crop was planted one year after oil applications had ceased, soil oil contents ranged from 2.4 to 7.3% and barley growth ranged from excellent to nil thus presenting an excellent opportunity to make a quantitative determination of growth-limiting oil contents and the role of other soil factors in plant growth inhibition.

Growth of barley in the second year was similar to that in the previous year, but the results indicated that good growth was possible if oil contents were below 4%. In the 2.5-4% range, growth was highly variable and it appeared that salt concentrations were acting synergistically with oil-induced stress to inhibit growth. Measures were then taken to reduce both oil contents and salt concentrations in the root zone. These included deep ripping to shatter the clayey subsoil, heavy nitrogen fertilization to enhance microbial degradation of the hydrocarbons and application of manure as a general soil amendment. These practices resulted in greatly improved barley biomass production in the third growing season with large decreases in electrical conductivity, chlorides and other ions as well as decreases in soil oil content. Application of manure resulted in a 2.4 fold growth increase although manure had no demonstrable effect on oil degradation or on the other chemical parameters measured.

As in some plots barley growth was still less than 1% of the growth on oil-free soil, the three remedial treatments were applied again after harvesting the third crop. This final attempt at reclamation of the oil treated soils was very successful as in the fourth year plant growth was virtually uniform regardless of oil treatment history and yields were similar to those on oil-free soil. For example, growth in a plot in which the yield was 29 g $m^{-2}$ in the third year increased 592 g $m^{-2}$ in fourth year, a 20-fold change. It was clearly shown barley could be grown in soils containing up to 4.5% of well-weathered oily wastes when salt concentrations were low (~ 2 dS $m^{-1}$).

In order to plan for future land uses of areas used for land treatment of oily wastes, the barley at Lloydminster was analyzed to determine if the plants had taken up toxic organic chemicals or heavy metals. A method was developed to extract organic compounds (acidic, basic, aliphatic, aromatic and polar fractions) from plant material and was used to analyze green fresh-frozen and mature air-dry straw and grain. A larger number of compounds were detected in the fresh-frozen samples than in the air-dry samples. Nearly all the substances contained hydroxyl, aldehydic and/or carboxylic acid functional groups. Almost

all the compounds were naturally occurring plant components or derived from natural products. It was unlikely that plant uptake from the soil was responsible for the presence of any of the compounds detected and there was a complete absence of toxic compounds that would render the crops unsuitable for animal or human consumption. Heavy metals were in similar concentrations in treated and untreated soils as well as in grain and straw grown in oily and oil-free soils.

Surface water runoff ponds initially became contaminated with mobile ions such as chloride, but runoff water generally met Canadian Drinking Water Standards. Concentrations of chloride, nitrate, and sulphate gradually decreased at Lloydminster and at the end of the study the water met drinking water standards.

Groundwater at some sites became contaminated with chlorides and nitrates which originated from the sludges and fertilizer respectively. Detailed studies at Lloydminster showed that inorganic contamination decreased rapidly with depth and posed no major threat to water quality.

There did not appear to be any groundwater contamination with hydrocarbons at any site based upon total carbon analyses. At Lloydminster samples taken in 1988 from wells constructed of stainless steel and teflon indicated trace amounts (50 $\mu g\ L^{-1}$) of hydrocarbons had reached the groundwater. When the wells were resampled in 1989 no hydrocarbons were detected in the water indicating the organics from land treatment sites pose no threat to groundwater quality.

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## 1. INTRODUCTION

The alternatives for the disposal of nonrecyclable, potentially toxic oily wastes generated in the oil and associated industries are currently limited to incineration, deep-well injection, burial in chemically secure landfills and land treatment (landfarming or soil biodegradation) (Bartha, 1986). Other methods, such as road oiling have been used as a functional disposal method but objections may be raised for environmental reasons. Of the above methods, incineration and land treatment aim to truly dispose of, i.e., totally degrade, the hydrocarbon constituents, whereas the other two methods seek to essentially contain the waste products in unaltered forms for perpetuity. Clearly, total deactivation/decomposition by thermal or biological means are preferred methods to the uncertainties of sub-surface containment.

In Canada in the year 1980, it was reported that landfills accounted for the disposal of 36% of the oily refinery wastes, land treatment 18%, incineration 7%, and deep well injection 1% (PACE Report 80-4, cited in Bulman et al., 1989). As land treatment was stated to be the least costly of these methods (12% of incineration costs), this technologically simple method has great appeal by producers of oily wastes. However, land treatment is unsuitable for many waste products, such as those that have limited biodegradable properties, those that contain excessive amounts of heavy metals or those that are highly saline.

In Alberta, large amounts of non-refinery oilfield production wastes are generated which should be suitable for disposal by land treatment. These include tank bottom sludges, separator sludges, slop oils and hydrocarbon contaminated soils which together amount to 100,000 to 200,000 $m^3$ produced per year (Peake et al., 1985). Many of these oily wastes are currently processed by oilfield reclamation plants which extract the useable oil products with the concomitant production of a lesser volume of unusable hydrocarbon waste. This study was designed to determine if raw oilfield wastes or those from

reclaiming plants in Alberta could be successfully and safely disposed of by land treatment in Alberta soils under cool continental climatic conditions.

The determination of land treatment feasibility involves factors other than capital and operating costs and rates of biodegradation. It is essential that the introduction of oily wastes into soils does not adversely affect surface water or groundwater quality or prevent revegetation for future food or fiber production, erosion control or amenity plantings. To prevent these effects sludge material must be screened carefully to make sure the materials are suitable for land treatment, i.e., low toxicity potential, biodegradability, and low in salts and metals. Surface water can be protected by proper site design and location (e.g., protective barriers) and groundwater by selection of low permeability subsoil and low mobility sludges. In any case, water quality must be monitored to determine if contamination is occurring.

It is desirable to enhance hydrocarbon biodegradation rates as loading levels can be increased and, if desired, sites can be more rapidly reclaimed for other uses. As the process is microbiologically driven, the strategy is to optimize conditions which increase microbial activity. Oily sludges are rich in organic substrates but practically devoid of essential mineral nutrients which must be provided by the soil. The introduction of carbon-rich, nutrient-poor substrates into soils necessitate additions of nitrogen and phosphorus to maintain microbial metabolism at reasonable rates. As the microbial community will place excessive demands on nitrogen and phosphorus in hydrocarbon-containing soils, additional soluble fertilizer sources must be provided if planting of the areas is part of the land use plan.

Aside from fertilization, the other common measure taken to enhance degradation is frequent cultivation. This serves to homogenize the sludges, and prevent the formation of low reactivity clods in the soil, and to increase soil aeration. The biodegradation process is largely an aerobic process performed by the bacterial microflora (Sung et al., 1986) and the presence of poor soil structure or waterlogging will greatly inhibit hydrocarbon decomposition.

The application of excessive amounts of oily wastes may also result in poor soil physical structure, reduced water infiltration, and promote anaerobic conditions. Thus repeated moderate applications of both hydrocarbons and soluble fertilizers will result in the most efficient land treatment operations.

Rehabilitation of soils that have received repeated treatments of hydrocarbon wastes has generally not been attempted (Bossert and Bartha, 1985). It has been suggested that such soils should not be used for animal or human food production (Bartha, 1986) but the chemical risks associated with crops grown on former land treatment sites have never been assessed. It would seem reasonable that when land treatment sites are decommissioned, that not only should the soils be capable of supporting plant growth, but that the plant biomass should be safe for consumption by humans, domestic grazers, or wildlife.

This report is a summary of an eight year study on the feasibility of using the land treatment technique for the disposal of oily sludges in Alberta. Oily wastes were repeatedly applied to soils and the oil content of the soils monitored. Risk assessments have been made on surface water and groundwater, inputs of heavy metals and salts, the potential for rehabilitating land treatment sites, and the potential for growing crops on decommissioned sites. Further details on many aspects of the study can be found in previous reports (Peake et al., 1985; Peake and Connery, 1986; Danielson et al., 1987, 1988, and 1989).

## 2. STUDY OBJECTIVES

The research was conducted in two phases; a sludge Application/ Degradation monitoring phase in the period of 1982 through 1985 and a Degradation/Reclamation phase in the years 1986 through 1989. The overall objective was to determine if the land treatment process was feasible for the disposal of oily waste sludges under Alberta conditions and if the practice resulted in any environmental hazards. Specifically, the objectives of Phase 1 - Application/ Degradation were:

1. To select four diverse climatic sites in Alberta, construct demonstration plots and to apply different rates of oily sludges to the soils.

2. To determine the rates of degradation of the sludges over a one to four year period.

3. To determine whether the application of different levels of mineral fertilizer would influence degradation rates in the demonstration plots.

4. To determine if the frequency of cultivation would influence sludge degradation rates.

5. To determine if either surface waters or ground waters were subject to contamination by the oily sludge or its decomposition products or by inorganic ions.

In Phase 2 - Degradation/Reclamation, intensive studies were limited to one of the four sites (Lloydminster). All sites were tested for their ability to support crop growth following land treatment but only at Lloydminster were reclamation efforts made to enhance soil productivity. In general, then, the objective of this phase of the study was to determine if land treatment sites could be returned to agricultural use and to assess the risks of land treatment on soils, crops and water. The specific objective of the Degradation/Reclamation Phase were:

1. To continue monitoring the degradation of previously applied oily sludges.

2. To chemically characterize the hydrocarbons remaining in the soil and to determine if refractor compounds had accumulated.

3. To determine if soils treated with oily sludges could be returned to normal agricultural use.

4. To determine the quantitative relationship between soil oil content and crop production.

5. To apply standard agricultural practices to the Lloydminister site to reclaim the soil for crop production.

6. To develop a technique for assessing the uptake of aromatic hydrocarbons by plants and to assess the uptake of potentially dangerous compounds by agricultural crops.

7. To determine if treated soils or crops grown on oily soils contained excessive amounts of heavy metals.

8. To determine the effects of land treatment on surface and groundwater quality.

9. To chemically degrade asphaltenes to determine if biological degradation would release potential contaminants of groundwater or toxic compounds.

10. To analyze the upper soil profile of the Lloydminster site for specific, potentially toxic aromatic compounds which might migrate into the groundwater.

# 3. METHODS AND MATERIALS

## 3.1 SITES AND PLOT ESTABLISHMENT

Study sites were selected in four geographic areas of Alberta in which oily wastes were produced (Figure 1). These sites varied climatically (Table 1), in soil properties, and in the source and type of the oily wastes (Peake et al., 1985). The Lloydminster site was located close to the source of heavy oil wastes and the latter three sites were adjacent to oilfield reclaiming plants which produce chemically untreatable oil wastes.

The four sites, in order of overall study intensity, were:

1. Lloydminster, in a field under small grain cultivation; provided by Husky Oil Ltd.
2. Drayton Valley, on a recently cleared woodland site in the midst of a commercial land treatment operation; provided by Pembina Oilfield Separators, Ltd.
3. Grande Prairie, in an agricultural field devoted to hay production; provided by Nalcan Cleaning and Disposal Ltd., and
4. Brooks, in a permanent dryland pasture; provided by Anric Reclaimers Ltd.

The Lloydminster site was in the black soil zone and was a loam (38% sand, 16% clay, 46% silt), and the Brooks site, a sandy loam (54% sand, 14% clay, 32% silt), consisting of orthic brown solods. The Grande Prairie soil was a fine sandy loam (54% sand, 12% clay, 34% silt) with SIC varves underlaid with clay and the Drayton Valley site was a grey-wooded soil, with a clay loam texture (42% sand, 24% clay, 24% silt).

At each site, demonstration plots were established in 1982 and consisted of a suite of eight treatment plots, each 9.1 x 30 m (Figure 2). The sites were almost flat with a slight gradient to a surface water catchment pond to prevent flooding and to monitor surface water quality. A groundwater monitoring well was established in the centre of each site. Additional wells and piezometers were established

Figure 1. Location of land treatment demonstration plots in Alberta.

Table 1. Climatic data for the sites of oily sludge land treatment demonstration plots.

| Site | Location | Elevation m | Frost-Free Period days | Mean Annual Temp. °C | Mean Annual Precip. mm |
|---|---|---|---|---|---|
| Brooks | 50°33'N 111°50'W | 760 | 116 | 3.8 | 335 |
| Grande Prairie | 55°07'N 118°58'W | 655 | 108 | 1.2 | 453 |
| Drayton Valley[1] | 53°12'N 114°58'W | 720 | 111 | 2.2 | 492 |
| Lloydminster | 53°17'N 110°04'W | 649 | 120 | 1.6 | 425 |

[1] Calmar station data

at the Lloydminster site in 1986 and 1987 to obtain detailed information on groundwater (see Section 3.5). In 1983, the eight plots at each site were subdivided in half to provide additional treatments giving 16 plots (15 x 9 m) at each site. No formal control plots were established and either the pre-treatment data or data from the border areas or adjacent fields were used for no-treatment comparisons.

## 3.2 DEMONSTRATION PLOT TREATMENTS

### 3.2.1 Oily Sludge

The main treatment was the amount of oily sludge applied, which varied both within years, among years and among sites. The amount of hydrocarbons applied could not be precisely controlled due to extremely variable nature of the sludges, although initially the aim was to apply enough in 1982 to give 2 and 4% oil contents in the soil. The quality (oil, water, salt and solid content) of the sludges at each site varied considerably due to the waste product nature and actual rates of oil applications were largely determined by post-application

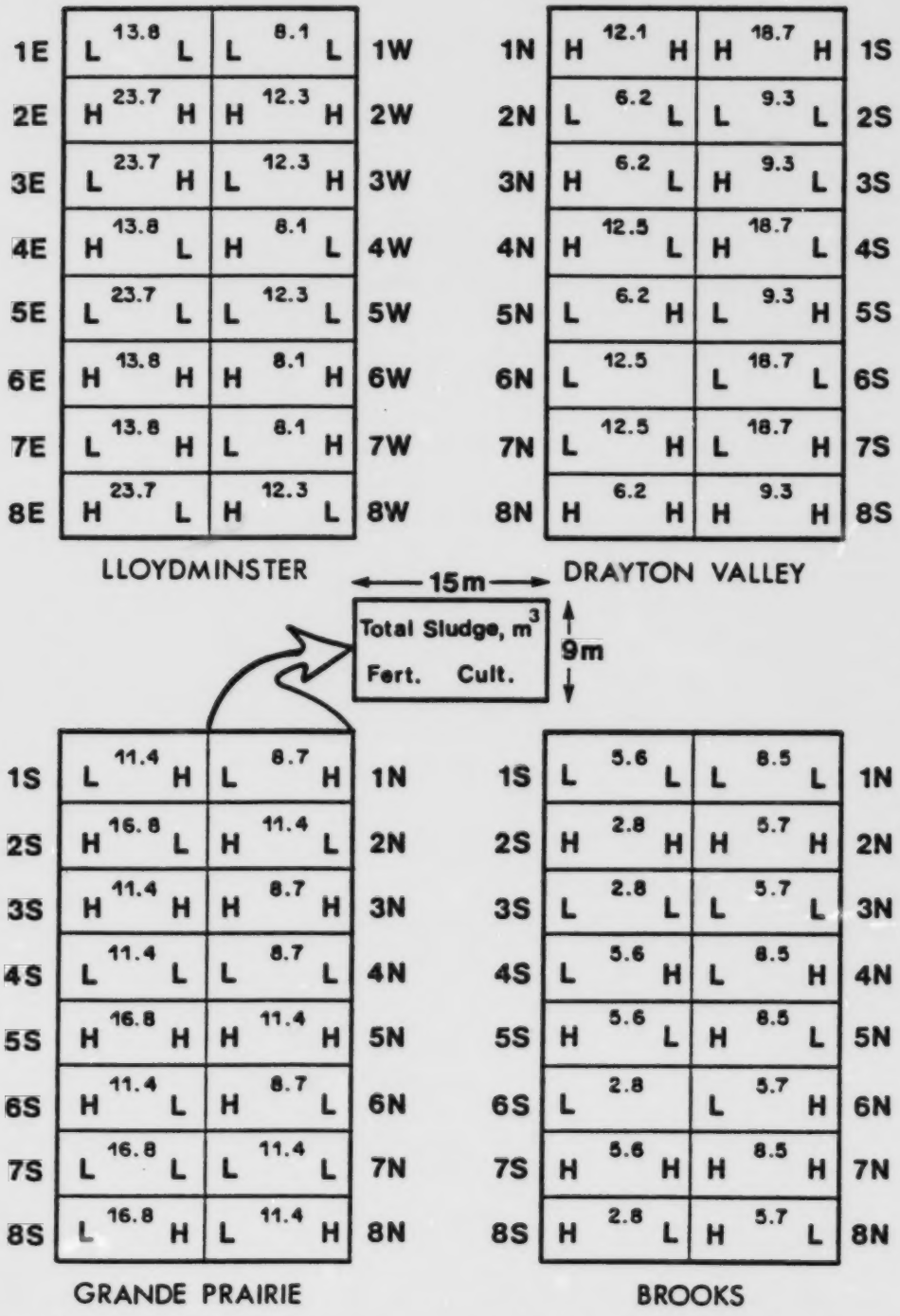
1E L 13.8 L L 8.1 L 1W
2E H 23.7 H H 12.3 H 2W
3E L 23.7 H L 12.3 H 3W
4E H 13.8 L H 8.1 L 4W
5E L 23.7 L L 12.3 L 5W
6E H 13.8 H H 8.1 H 6W
7E L 13.8 H L 8.1 H 7W
8E H 23.7 L H 12.3 L 8W
LLOYDMINSTER
1N H 12.1 H H 18.7 H 1S
2N L 6.2 L L 9.3 L 2S
3N H 6.2 L H 9.3 L 3S
4N H 12.5 L H 18.7 L 4S
5N L 6.2 H L 9.3 H 5S
6N L 12.5 L 18.7 L 6S
7N L 12.5 H L 18.7 H 7S
8N H 6.2 H H 9.3 H 8S
DRAYTON VALLEY
15m
Total Sludge, m3
Fert. Cult.
9m
1S L 11.4 H L 8.7 H 1N
2S H 16.8 L H 11.4 L 2N
3S H 11.4 H H 8.7 H 3N
4S L 11.4 L L 8.7 L 4N
5S H 16.8 H H 11.4 H 5N
6S H 11.4 L H 8.7 L 6N
7S L 16.8 L L 11.4 L 7N
8S L 16.8 H L 11.4 H 8N
GRANDE PRAIRIE
1S L 5.6 L L 8.5 L 1N
2S H 2.8 H H 5.7 H 2N
3S L 2.8 L L 5.7 L 3N
4S L 5.6 H L 8.5 H 4N
5S H 5.6 L H 8.5 L 5N
6S L 2.8 L 5.7 H 6N
7S H 5.6 H H 8.5 H 7N
8S H 2.8 L H 5.7 L 8N
BROOKS

Figure 2. Demonstration plot arrangement and total sludge, applications, fertilizer and cultivation treatments at each of the four land treatment sites.

soil analyses. The chemical composition of the sludges was also variable and representative analyses of sludges applied in 1982 are given in Tables 2 and 3 and detailed analysis of the aromatic fraction of one sludge given in Table 4. Additional details on sludge composition can be found in Peake et al. (1985).

Two rates of sludges were applied to plots at Lloydminster, Grande Prairie and Drayton Valley in 1982 and to the Brooks plots in 1983. One year later the eight plots were divided in half and an additional two rates were applied to one half of the plots at each site. At two sites (Brooks and Drayton Valley) either one or two sludge applications were made, at Grande Prairie two or three applications and at Lloydminster either three or four applications were made. Times and quantities of the applications are given in Tables 6, 12, 18, and 21. At the three reclaiming sites, all the sludges were taken from the same respective sludge ponds each year and at Lloydminster tank bottom sludge was applied in 1982 and 1983 and slop oil in 1984 and 1985.

Table 2. Composition and acidity of waste oils and sludges selected for land treatment at four sites.

| Source | Oil % | Water % | Solids % | pH |
|---|---|---|---|---|
| Brooks | 31.9 | 21.9 | 46.2 | 7.1 |
| Drayton Valley | 9.3 | 16.6 | 74.1 | 7.8 |
| Grande Prairie | 21.0 | 34.2 | 44.7 | 10.1 |
| Lloydminster | 11.5 | 4.5 | 83.9 | 8.5 |

Table 3. Percent composition of oils extracted from oily sludges applied to land treatment sites.

| | Grande Prairie | Drayton Valley | Brooks | Lloyd-minster |
|---|---|---|---|---|
| Aliphatics | 74 | 66 | 43 | 38 |
| Aromatics | 10 | 10 | 20 | 15 |
| Neutral Nitrogen | 5 | 8 | 16 | 17 |
| Resins | 7 | 10 | 8 | 13 |
| Asphaltenes | 4 | 6 | 13 | 17 |

3.2.2 Fertilizer and Lime

Two levels of fertilization were used to enhance microbial degradation of the waste hydrocarbons in the Application/Degradation phase (1982-1985). These were initially the same at all sites and equivalent to 230 and 460 kg N $ha^{-1}$ $yr^{-1}$. The actual application at the low rate on one 9 x 30 m plot was 16.7 kg 34-0-0 and 3.2 kg 16-20-0. The high rate was discontinued after 1983 and all plots were fertilized at the low rate up to 1986. In the 1986 to 1989 period the rate was dependent upon local fertilization or reclamation practices and are specified in Table 5.

Lime was added to all soils in 1982 to ensure that the soils were weakly alkaline to prevent possible leaching of heavy metals. Amounts added are given by Peake et al. (1985).

3.2.3 Cultivation Frequency

At all sites, half the plots were cultivated either once every two weeks or once every four weeks in 1982 and 1983 and once every four weeks until the end of Phase 1. After crops were planted, the areas were cultivated prior to planting. Cultivation consisted of rototilling the soil/sludge mixtures to a depth of about 15 cm.

Table 4. Composition of the aromatic hydrocarbon fraction from an oily sludge sample from the Brooks sludge pond.

| m/e | Compound | Percent |
|---|---|---|
| 142 | C1-naphthalenes | 0.76 |
| 156 | C2-naphthalenes | 7.88 |
| 170 | C3-naphthalenes | 10.25 |
| 184 | C4-naphthalenes | 4.42 |
| 154 | biphenyl | 0.28 |
| 166 | fluorene | 0.78 |
| 168 | C1-biphenyl | 0.48 |
| 180 | C1-fluorenes | 2.44 |
| 194 | C2-fluorenes | 2.19 |
| 208 | C3-fluorenes | 0.30 |
| 178 | phenanthrene | 1.87 |
| 192 | C1-phenanthrenes | 4.95 |
| 206 | C2-phenanthrenes | 5.64 |
| 220 | C3-phenanthrenes | 3.42 |
| 234 | C4-phenanthrenes | 1.19 |
| 184 | dibenzothiophene | 9.92 |
| 198 | C1-dibenzothiophenes | 5.34 |
| 212 | C2-dibenzothiophenes | 7.00 |
| 226 | C3-dibenzothiophenes | 6.27 |
| 234 | benzonaphthothiophene | 1.08 |
| 248 | C1-benzonaphthothiophene | 0.91 |
| 262 | C2-benzonaphthothiophene | 0.25 |
| 202 | fluoranthene | 2.60 |
| 202 | pyrene | 2.48 |
| 216 | benzofluorenes and C1-mass 202 | 1.10 |
| 230 | C1-mass 216 compounds | 0.14 |
| 228 | benz(a)anthracene | 0.70 |
| 228 | chrysene and triphenylene | 1.26 |
| 242 | C1-mass 228 compounds | 0.31 |
| 252 | benzofluoranthenes | 0.84 |
| 252 | benzo(e)pyrene | 0.22 |
| 252 | benzo(a)pyrene | 0.25 |
| 252 | perylene | 0.11 |
| 254 | | 0.03 |
| | other aromatic compounds | 12.34 |

## 3.3 SOIL ANALYSES

### 3.3.1 Soil Sampling

Five replicate samples were removed from each plot (eight plots per site in 1982, 16 after 1982) for determinations of oil content, soil oil composition and inorganic chemistry. In 1982 the five samples were selected randomly, and thereafter the same pre-selected sample points were used for repeated sampling to minimize variability and edge effects. Five samples from the 0 - 15 cm depth at each sample point were combined, the samples mixed and analysed. Prior to 1986 the samples were not sieved, but thereafter all samples were sieved through a 4 mm sieve for inorganic analyses and through a 2 mm sieve for oil analyses.

During the Application/Degradation Phase samples were taken from each site prior to spring sludge applications, immediately following applications and at least once more at the end of the growing season. Precise dates of sampling are given in Peake et al. (1985) and Peake and Connery (1986) but only yearly means will be reported here. In the 1986-1989 period samples were taken in the same manner at the same points but only in the fall of each year (no samples taken at Brooks and Grande Prairie). Some additional surface samples and cores were taken and are detailed in previously reports or in the Results section.

### 3.3.2 Oil Content

The oil content of the soil was determined by extraction of the soil with toluene into Soxhlet extractor with a Dean-Stark apparatus for collection of water in the sample. Solvent was removed from the soil by drying and the carbon content determineed using a Leco Carbon Analyser. The difference in carbon content between extracted and non-extracted soils was converted to oil weight by dividing by 0.83. All soil oil concentrations are expressed as percent oil in the soil based on the weight of soil following carbon determinations, i.e., water and organic matter free. This is the same as the oil:solids

ratio (x100) used in some previous reports (e.g. Peake et al., 1985; Danielson et al., 1988). The total amount of oil in the soil was based on a 15 cm deep layer weighing 2.2 x $10^6$ kg $ha^{-1}$.

### 3.3.3 Asphaltene Content

Asphaltenes were determined by extraction of soil with toluene and rotary evaporation of the solvent. The oil was redissolved in toluene (1 g oil: 1 mL toluene) and the asphaltenes precipitated by adding a 10-fold excess of hexane. The asphaltenes were collected by filtration and weighed.

### 3.3.4 Oil Composition

Oil was extracted with toluene, redissolved and the asphaltenes precipitated as above. The solvent was evaporated from the remaining maltene fraction which was then chromatographed on silica gel to separate the oils from the resins. First hexane, followed by methylene chloride and finally freshly distilled tetrahydrofuran were used to elute the oils, a less polar and a more polar resin fraction, respectively. All solvents were removed by rotary evaporation to constant weights. The oils were further fractionated into aliphatics and aromatics by chromatography on alumina with pentane as the eluent for the aliphatics and benzene for the aromatics. Detailed analysis of the aromatic fraction was done by GC/MS.

### 3.3.5 Chemical Degradation of Asphaltenes

Depolymerization is a degradative technique developed by Gould (1978) to aid in the structural analysis of coal. Depolymerization using phenol and an acid catalyst, para-toluene sulfonic acid, degrades complex organic structures by removing aliphatic sidechains and linkages from and between aromatic nuclei. The aromatic units, no longer incorporated into high molecular weight structures, can be isolated and identified. In a sense, this is a chemical mimicry of biodegradation which occurs more readily on aliphatic hydrocarbons; the aromatic hydrocarbons are less easily metabolized so will persist longer in the soil. Both chemical and biological degradation processes act preferentially upon the aliphatic moieties and the aromatic

moieties released by the two processes will probably be of different forms. The depolymerization produces unsubstituted aromatics, while biodegradation likely generates quinones or hydroxy-substituted aromatics. The chemical degradation technique gives a more rapid estimate of the type of degradation products then a lengthy microbial incubation.

In 1987 samples from one plot at Lloydminster were selected to chemically degrade the asphaltene fraction of the soil oil and to identify the mobile degradation products as a predictor of potential contamination of water with toxic compounds. Basically soil samples from Plot 6E containing 5.0% hydrocarbons were extracted with toluene, and the oil fractionated and depolymerized. The depolymerized products were further fractionized and select samples were analysed by GC/MS. Detailed chemical procedures are reported by Danielson et al. (1988).

### 3.3.6 Inorganic Soil Chemistry

In the Application/Degradation phase surface soils and shallow cores were analysed for pH, SAR, Ec, water extractable ions and heavy metals using standard methods (McKeague 1978). In the Degradation/Reclamation phase surface soils (0-15 cm) were analysed by the Earth Sciences Division, Alberta Environment for pH and soluble salts in a saturated paste, extractable cations and anions from saturated extracts and Ec, SAR, and total C. Available N and P were estimated by extraction of $NO_3$-N with 0.01 N $CuSO_4$ + 0.007 N $Ag_2SO_4$, $NH_4$-N with 2 N KCl and P with 0.03 N $H_2SO_4$ + 0.03 N $NH_4F$. Heavy metals (Fe, Cu, Zn, Pb, Mn, Cd and Ni) were estimated in DTPA soil extracts from Lloydminster soils in 1987. In the Degradation/Reclamation Phase soil samples were taken from the clip plots used to estimate primary productivity (Section 3.4.2) in order to correlate plant growth and soil chemistry.

### 3.3.7 Migration of Contaminants in the Upper Solum

In 1985, soil cores were taken from the Lloydminster plots, which received the largest quantities of oily sludges, to determine if oil or mobile inorganic ions migrated down the soil profile. Measurements were made to a depth of 150 cm and analyses done as in previous sections.

In 1989 samples were taken from Plot 8E, which contained the highest level of oil of all the plots at Lloydminster, for further migration analyses and to determine if specific aromatic compounds were present. Duplicate samples were taken from the 0-15, 15-30 and 30-45 cm depths. The 0-30 cm depth constituted the root zone of barley and other crops. An abrupt change occurred at 30 cm and below this depth was subsoil consisting of hard, very compact clay. The six samples were extracted with toluene in a modified Soxhlet-Dean Stark apparatus to separate the oil. Each extract was divided into two equal portions; one for analysis for target compounds, and the other to determine the oil content of the soil. Prior to analysis of the oil by GC/MS, deuterated internal standards were added and the aliphatic components and asphaltenes were separated by column chromatography. The solvent was removed by rotary evaporation from the second portion and the oil was weighed. The samples were analysed by GC/MS following extraction and fractionation (as above) for dibenzothiophene, pyridine, carbazole, 2-methyl naphthalene, biphenyl, acridine, 4-methyl biphenyl and 9-ethyl fluorene. Inorganic salts were also determined by The Earth Sciences Division, Alberta Environment.

## 3.4 PLANT PRODUCTIVITY

### 3.4.1 Planting of Demonstration Plots

All four land treatment sites were planted in June 1986. The selection of crops and fertilizer levels were determined by local farming practices and appropriate to each region. The entire plot areas as well as the surrounding buffer zones were cultivated, fertilized and planted. The buffer zones were planted to provide control areas free of oily sludges to determine the effect of the 16 sludge-cultivation-fertilization treatments on crop yield. The Drayton Valley and Grande Prairie sites were planted to perennial hay crops, Brooks to perennial dryland pasture and were not treated further (Table 5). The Lloydminster site was planted to barley four years in succession with an adjacent field serving as a control.

Table 5. Crops planted on the four land treatment sites, cultivation measures and fertilizers applied in the Degradation/ Reclamation Phase (1986-1989).

| Site[1] (Planting date) | Cultivation | Fertilizer | Seed |
|---|---|---|---|
| Lloydminster (June 9, 1986) | Rototilled | 27:27:0 80 kg $ha^{-1}$ | Bonanza barley |
| Lloydminster (May 14, 1987) | Rototilled | 39kg 46:0:0 20 kg 11:51:0 | Leduc barley |
| Lloydminster (May 18, 1988 | Subsoiled Rototilled | 120 kg 35:0:0 | Samson barley |
| Lloydminster (June 4, 1989) | Rototilled (Subsoiled, Fall 88) | 40 kg 17:20:0 (120 kg 34:0:0, Fall 1988) | Samson barley |
| Drayton Valley (June 10, 1986) | Harrowing | 16:20:0 34:0:0 50 kg $ha^{-1}$ each | 30% Creeping red fescue 30% Richmond timothy 20% Alsike clover 20% Meadow foxtail |
| Grande Prairie (June 17, 1986) | Harrowing | 12:15:0 50 kg $ha^{-1}$ | 10 lb Alfalfa 4 lb Timothy |
| Brooks (June 18, 1986) | Harrowing | 11:51:0, 50 kg 34:0:0, 25 kg | 40% Crested wheatgrass 40% Russian wild rye 20% Sainfoin |

[1] All of site areas at Lloydminster, Grande Prairie, and Brooks, including borders were cultivated and planted. Plots 24,000 $ft^2$ (2230 $m^2$), borders approximately 7000 $ft^2$ (650 $m^2$).

Only the plot area at Drayton Valley was planted.

### 3.4.2 Productivity Assessments

Subjective estimates of plant productivity were made at all four sites in 1986 and 1987 by observing crop growth in each plot and rating growth from poor to excellent. Comparisons were made with the same crops growing on oil-free soil where possible. Where more than one species had been planted in 1986, the successful species were recorded.

Quantitative estimates of plant growth were made at Lloydminster and to a limited degree, at Drayton Valley. One meter square areas were established at the same five replicate points per plot that were used for soil sampling and the vegetation clipped at the groundline. The plant material was air-dried, separated into straw and grain and weighed. In 1989, one-quarter meter square plots were used due to the lush growth of the barley at Lloydminster.

### 3.4.3 Plant Uptake of Heavy Metals and Hydrocarbon Contaminants

Heavy metals contents of barley straw and grain were determined in 1987 from Lloydminster plots which exhibited fair and good growth and from plants growing in uncontaminated soil. Analyses were performed on five replicates from each treatment by the Earth Sciences Division.

Ten barley samples were taken in 1988 to determine if plants growing on oily sludge treated soils had taken up undesirable organic compounds which would render the crop unsuitable for human or livestock consumption. Both immature and mature grain and straw was sampled to maximize the chance of detecting contaminants. All plants were washed with distilled water to remove any surface debris and straw close to base was avoided. Immature green plants (five replicates per treatment) were sampled July 29 from Plot 5W (soil oil content 3.1%, barley yeild 53% of control), Plot 8W (oil content 2.7%, yield 82% of control) and from the adjacent oil-free field. The plants were washed with distilled water and frozen until analyses could be performed. Mature plants ready for harvest were sampled August 25 from Plot 4E (oil content 4.1%, plant growth 35% of control) and the adjacent field.

Grain and straw were separated and the mature samples were ground in a Wiley Mill and the immature samples were fragmented in a blender. Two grams of plant material from each of the five replicate field samples were combined and the samples were homogenized in acetonitrile. The samples were extracted with acetonitrite and the extracts separated into acidic, basic, aliphatic, aromatic and polar fractions (details of separation procedure in Danielson et al., 1988). All plant samples were analysed by GC/MS. Analyses were carried out on a Hewlett-Packard 5890 Gas Chromatograph coupled with a 5970 Mass Selective Detector. Standards consisted of known concentrations of a variety of aliphatics, aromatics and aliphatic acids.

### 3.4.4 Recovery of Spiked Components From Barley

Deuterated compounds ("spikes") were added to a grain sample to determine the effectiveness of the extraction/detection procedure for determining the potential plant uptake of organic contaminants. Barley seed collected from plot 4W at Lloydminster in 1986 were ground using a Wiley mill with 1 mm mesh size. Four 5 g samples were each spiked with seven deuterated standards representing four classes of organic compounds: acidic, basic, aliphatic, and aromatic. Equal amounts (500 µL) of naphthalene $d_8$, anthracene $d_{10}$, chrysene $d_{12}$, dibenzothiophene $d_8$, phenol $d_6$, quinoline $d_7$, and hexadecane $d_{34}$, all of approximately 1 mg $mL^{-1}$ concentration, were added to the four samples. Methylene chloride was added to each sample to allow the tracers to be evenly distributed by stirring.

Three subsamples were extracted with acetonitrile and sonification with a Brinkman Polytron Homogenizer and a fourth subsample was extracted with methylene chloride in a conventional Soxhlet apparatus. The four extracts were then fractionated into acidic, basic, aliphatic, aromatic and polar fractions which were analysed by capillary GC/FID. Details of the techniques are reported by Danielson et al. (1988).

### 3.4.5 Reclamation Procedures at Lloydminster

Aside from cultivation and fertilization, no attempts were made to improve soil properties at Brooks, Drayton Valley or Grande Prairie. However, at Lloydminster, attempts were made to rehabilitate

the site in 1988 and 1989, such that the land could be returned to agricultural use. The entire site was subsoiled with a Springdale subsoiler on May 7, 1988 to enhance leaching of salts from the root zone. The subsoil was broken up at a depth of 30-40 cm and, with the exception of the central plot area, very little subsoil was brought to the surface. On exposed subsoil blocky material, there was a very distinct transition from the Ap horizon to the clayey, hard subsoil. Following the deep ripping, fertilizer was applied to the entire plot area. The rate applied was 225 kg N $ha^{-1}$ of 35:0:0 $NH_4NO_3$ (120 kg actual application).

Well decomposed manure was applied to the west plots and to the west half of the east plots. The 7.5 m easternmost strip served to determine if the manure had any beneficial effects on plant growth. The manure was applied at approximately a rate of 40 tonnes $ha^{-1}$; the actual amount applied was four loads weighing about 6.5 tonnes each. The manure was dumped on the plots and spread with a blade and harrow.

On May 18, the entire area was thorougly rototilled and planted with Samson variety barley. The surrounding field that was used as a non-oil control was planted to barley at about the same time.

After the site had been sampled for productivity, it was cleared of vegetation in mid-October and the crop burned to eliminate barley seed which would interfere with the 1989 crop. As the ripping-fertilizer-manure treatments applied in May resulted in much improved plant performance, the same treatments were reapplied to further improve soil conditions and plant growth in the 1989 season. The entire area was deep ripped, fertilized with $NH_4NO_3$ (225 kg N $ha^{-1}$, 34:0:0) and manure was applied at a rate of 40 tonnes $ha^{-1}$. These treatments were applied in the fall as they, especially breaking up of the subsoil, are most effective when the soil is dry. In May of 1989 the entire area was rototilled, planted to barley and 17:20:0 fertilizer was applied at a rate of 75 kg $ha^{-1}$.

## 3.6 GROUNDWATER AND SURFACE WATER QUALITY

A single 6 m deep groundwater well was installed in the centre of each set of plots in 1982 and sealed with bentonite to prevent

surface contamination. Samples were taken prior to sludge applications, and monthly thereafter, except at Brooks where the well was dry. The parameters measured included total carbon, volatile carbon, organic carbon, Cl, $NO_3$, $SO_4$ and pH. The first four parameters could indicate contamination by the sludges and $NO_3$ could originate from fertilizers. The runoff pond was also frequently sampled to determine if surface waters were susceptible to organic or inorganic contamination.

In the Degradation/Reclamation Phase groundwaters were intensively studied at the Lloydminster site. Fifteen piezometers and seven water table wells were installed on the plot area (for installation details see Danielson et al., 1989). Two water table wells were constructed using stainless steel and teflon materials and equipped with dedicated sampling hoses to sample for hydrocarbon contamination. Measurements were taken from 1986 to 1989 to establish shallow groundwater flow and groundwater chemistry. Chemical measurements were similar to those made prior to 1986 except water samples from the stainless steel wells were scanned for total hydrocarbons in 1988 and analysed by GC/MS for aromatic compounds in 1989. In addition, water was analysed for heavy metals and a full range of cations and anions. Surface water in the runoff pond was analysed for the same ions once per year.

## 4. RESULTS - FERTILIZER AND CULTIVATION AT ALL SITES

At no stage in the program were differences detected that could be attributed to the cultivation or fertilizer treatments (Peake et al., 1985). Although these may be important factors in influencing degradation rates, the variability encountered in the field plots may have precluded the detection of real differences. No further consideration will be given to the cultivation and fertilization treatments applied in the Application/Degradation Phase in 1982 and 1983.

Following 1983 all sludge treatments were fertilized and cultivated with equal intensity. As a result, much of the data collected has been summarized by the quantities of oily sludges applied to the plots. This was done either by (1) the number of applications, as at all sites the second application was made to only one-half of the plots resulting in two "number of application treatments" at each site, or by (2) sludge loading factors. As the cultivation and fertilization treatments are ignored, the result is four quantities of sludge applied to four replicate plots at each site. As the quantities vary at each site, the sludge treatments were assigned sludge loading factors ranging from 1 (low) to 4 (high) plus 0 loading for the control.

# 5. RESULTS - GRANDE PRAIRIE

## 5.1 APPLICATION/DEGRADATION PHASE 1982-1984

### 5.1.1 Oily Sludge Degradation

Although the range of intended sludge applications was 2-fold, 8.7 to 16.8 $m^3$, Table 6), the actual initial oil contents in all plots were similar (2.5 to 3%, Figure 3). Degradation (plus volatilization) in the first season was very rapid with an average 70% decrease in the oil contents in all plots. After a second application of sludge in 1983 to half the plots there was a 54% decrease in those plots and a 33% decrease in the plots treated only in 1982. Degradation rates in all treatments in 1984 were similar (44 - 49%) following a third application to all the plots. The percentage of oil degraded in the plots treated twice and those treated three times was identical, 71% of the total added over a three year period (Table 7).

### 5.1.2 Degradation of Aromatic Hydrocarbons

At the end of 1984, the oil extracted from the soil was analyzed for four aromatic hydrocarbons. About 99% of phenanthrene (m.w. 178) had disappeared over the 3 year period (Table 8). The higher molecular weight compounds pyrene (m.w. 202), chrysene (m.w. 228) and benzo(e)-pyrene (m.w. 252) were degraded to a lesser degree but still substantial quantities (>80%) had undergone biodegradation.

### 5.1.3 Groundwater and Surface Water Quality

There was no evidence that groundwater was contaminated with organic carbon over the three year monitoring period (Table 9). However, one year after the first sludge treatment was applied chloride and nitrate levels increased abruptly and continued to increase until the fall of 1984 when monitoring was terminated. The water in the surface runoff pond remained fairly constant in total carbon content (16-56 mg $L^{-1}$), chloride (11-78 mg $L^{-1}$), nitrate (0.1-35 mg $L^{-1}$), and sulphate (1-57 mg $L^{-1}$)concentrations over the 3 years with no indication of serious contamination (Peake et al. 1985).

Table 6. Grande Prairie land treatment plots: summary of oily sludge applications, cultivation and fertilizer treatments.

| Plot | Year sludge added | Sludge added yearly and total, m | Sludge loading factor[1] | Rate of: Ferti-lizer[2] | Rate of: Culti-vation[3] |
|---|---|---|---|---|---|
| 1N | 82,84 | 2.7 + 6 = 8.7 | 1 | Low | High |
| 1S | 82,83,84 | 2.7 + 2.7 + 6 = 11.4 | 3 | Low | High |
| 2N | 82,84 | 5.4 + 6 = 11.4 | 2 | High | Low |
| 2S | 82,83,84 | 5.4 + 5.4 + 6 = 16.8 | 4 | High | Low |
| 3N | 82,84 | 2.7 + 6 = 8.7 | 1 | High | High |
| 3S | 82,83,84 | 2.7 + 2.7 + 6 = 11.4 | 3 | High | High |
| 4N | 82,84 | 2.7 + 6 = 8.7 | 1 | Low | Low |
| 4S | 82,83,84 | 2.7 + 2.7 + 6 = 11.4 | 3 | Low | Low |
| 5N | 82,84 | 5.4 + 6 = 11.4 | 2 | High | High |
| 5S | 82,83,84 | 5.4 + 5.4 + 6 = 16.8 | 4 | High | High |
| 6N | 82,84 | 2.7 + 6 = 8.7 | 1 | High | Low |
| 6S | 82,83,84 | 2.7 + 2.7 + 6 = 11.4 | 3 | High | Low |
| 7N | 82,84 | 5.4 + 6 = 11.4 | 2 | Low | Low |
| 7S | 82,83,84 | 5.4 + 5.4 + 6 = 16.8 | 4 | Low | Low |
| 8N | 82,84 | 5.4 + 6 = 11.4 | 2 | Low | High |
| 8S | 82,83,84 | 5.4 + 5.4 + 6 = 16.8 | 4 | Low | High |

[1] Sludge loading factors range from low (1) to high (4).

[2] Low = 230 kg N $ha^{-1}$ in 1982, 1983 and 1984.

High = 460 kg N $ha^{-1}$ in 1982 and 1983, 230 kg N $ha^{-1}$ in 1984.

[3] High = Rototilling every 2 weeks in 1982 and 1983, every 4 weeks in 1984.

Low = Rototilling every 4 weeks in 1982, 1983 and 1984.

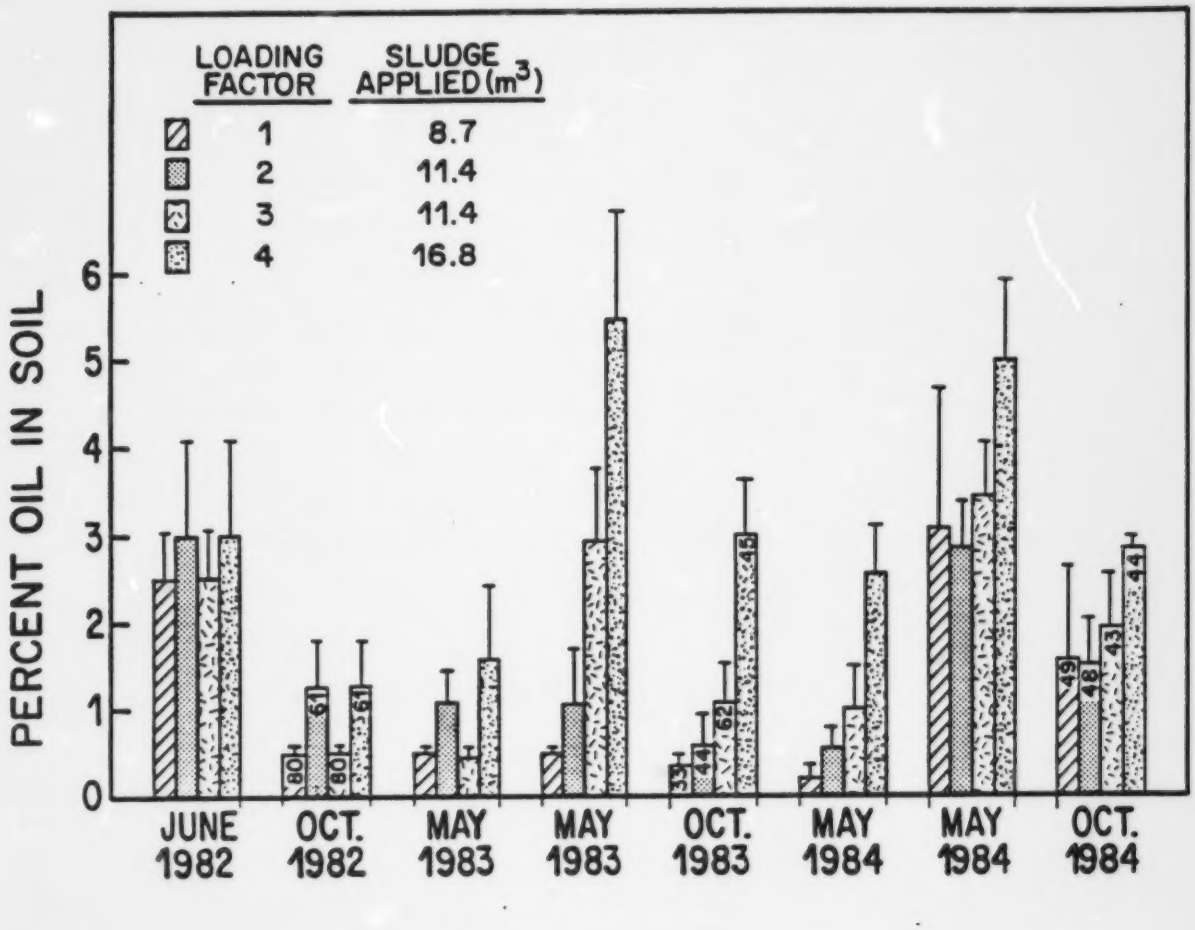


Figure 3. Oil content of soil at Grande Prairie with oil being added to all plots in 1982 and 1984 and to half the plots in 1983. Error bars are S.D., n = 4. Numbers in October bars indicate percent degradation from preceding May.

Table 7. Amount of oil applied as sludge to the Grande Prairie land treatment site and subsequent degradation.

| | Loading 3 and 4 | | Loading 1 and 2 | |
|---|---|---|---|---|
| | Oil added and degraded per year (kg $ha^{-1}$) | Percent oil in soil | Oil added and degraded per year (kg $ha^{-1}$) | Percent oil in soil |
| Oil added May 1982 | +60,000 | 2.7 | +60,000 | 2.7 |
| Oil degraded 1982/83 | -38,000 | | -43,000 | |
| Oil remaining May 1983 | 22,000 | 1.0 | 17,000 | 0.8 |
| Oil added 1983 | +70,000 | | 0 | |
| Oil present May 1983 | 92,000 | 4.2 | 17,000 | 0.8 |
| Oil degraded 1983/84 | -53,000 | | -9,000 | |
| Oil remaining May 1984 | 39,000 | 1.8 | 8,000 | 0.4 |
| Oil added 1984 | +53,000 | | +56,000 | |
| Oil present May 1984 | 92,000 | 4.2 | 65,000 | 3.0 |
| Oil degraded 1984 | -40,000 | | -31,000 | |
| Oil remaining Oct. 1984 | 52,000 | 2.4 | 34,000 | 1.5 |
| Total oil added | +182,000 | | +116,000 | |
| Total oil degraded | -130,000 | | -82,000 | |
| Overall degradation | 71% | | 71% | |

Table 8. Degradation of aromatic hydrocarbons over a three year period with annual sludge additions at Grande Prairie.

| Compound | m.w. | Total Amount Added (µg $g^{-1}$) | Amount Remaining (µg $g^{-1}$) | Percent Degradation |
|---|---|---|---|---|
| Phenanthrene | 178 | 270.0 | 0.6 | 99 |
| Pyrene | 202 | 13.1 | 2.6 | 80 |
| Chrysene | 228 | 21.8 | 2.4 | 89 |
| Benzo(e)pyrene | 252 | 7.5 | 1.1 | 85 |

5.1.4 Contaminant Migration in the Solum

The oily sludge was almost exclusively limited to the cultivation zone with very little vertical migration even after 3 years (Table 10). In contrast, chlorides were present in high levels throughout the 1.5 m of surface soil treated with oil. Nitrates were in very low concentrations in the solum of oil treated plots.

5.1.5 Soil Inorganic Chemistry

The pH of all plots remained above pH 7 throughout the monitoring period generally in the range of 7.6 to 8.5 (Peake et al., 1985). Heavy metal concentrations in the surface soil and amounts added to the most heavily treated plots as of October 1984 were 3.6 $\mu g\ g^{-1}$ Cu (6.0 kg $ha^{-1}$), 20 $\mu g\ g^{-1}$ Zn (40 kg $ha^{-1}$), 76 $\mu g\ g^{-1}$ Pb (150 kg $ha^{-1}$), 0.1 $\mu g\ g^{-1}$ Cd (0.2 kg $ha^{-1}$) and 1.2 $\mu g\ g^{-1}$ Ni (1.2 kg $ha^{-1}$). In October 1983 the SAR of the most heavily treated surface soils was 5.7 and the Ec was 7.7 dS $m^{-1}$.

5.2 DEGRADATION/RECLAMATION PHASE

5.2.1 Plant Growth

The growth of the hay crop planted in 1986 was poor in all sludge treatments in the first growing season (Table 11, Figure 4). Both alfalfa and timothy were present but the plants were scattered and small. In plots receiving the highest quantities of sludge the plants were chlorotic and had apparently stopped growing soon after emergence. Growth of alfalfa in a adjacent field was good. In the second year growth had substantially improved with alfalfa dominating on plots with low sludge loading factors and timothy dominating on the heavy application plots (Figure 5).

Table 9. Characteristics of groundwater at Grande Prairie taken from beneath oily sludge treated plots.

| Sample Date | Total Carbon | Volatile Carbon | Organic Carbon | Cl | $NO_3$ | $SO_4$ | pH |
|---|---|---|---|---|---|---|---|
| | | | $mg \cdot L^{-1}$ | | | | |
| June 1982 | 140 | 16 | 23 | 1.2 | <0.1 | 30 | 7.5 |
| August 1982 | 121 | 12 | 19 | 0.9 | <0.1 | <1 | 7.8 |
| October 1982 | 111 | 12 | 26 | 1.8 | 13 | 78 | 7.2 |
| June 1983 | 116 | 10 | 15 | 8.4 | 19 | 37 | 7.9 |
| August 1983 | 82 | 7 | 17 | 231 | 235 | 15 | 7.5 |
| October 1983 | 130 | 16 | 22 | 127 | 106 | 16 | 7.8 |
| June 1984 | 68 | 4 | 11 | 520 | 181 | 32 | 7.7 |
| October 1984 | 152 | 17 | 28 | 1383 | 406 | 20 | 7.5 |

Table 10. Concentrations of oil, Cl and $NO_3$ in 1984 in soil treated with oily sludge or in untreated soil at Grande Prairie.

| Depth (cm) | % Oil | | Cl mg $L^{-1}$ | | $NO_3$ mg $L^{-1}$ | |
|---|---|---|---|---|---|---|
| | Plots | Control | Plots | Control | Plots | Control |
| 0 - 15 | 2.30 | 0.05 | 134 | 2.6 | 1.4 | 13.5 |
| 15 - 30 | 2.69 | 0.02 | 138 | 2.0 | 1.7 | 6.5 |
| 30 - 60 | 0.09 | 0.01 | 710 | 3.9 | 0 | 8.0 |
| 60 - 90 | 0.03 | 0.02 | 773 | 2.6 | 0 | 2.7 |
| 90 - 120 | 0.04 | 0.02 | 490 | 1.4 | 2.0 | 0.8 |
| 120 - 150 | 0.02 | 0.02 | 239 | 1.6 | 8.4 | 1.3 |

Table 11. Visual estimates of the growth of alfalfa and timothy on the Grande Prairie land treatment site.

| Plot | Sludge loading factor | Crop Growth | |
|---|---|---|---|
| | | 1986 | 1987 |
| 1N | 1 | Poor | Fair |
| 3N | 1 | Very poor | Poor |
| 4N | 1 | Poor | Fair |
| 6N | 1 | Poor | Fair |
| 2N | 2 | Very poor | Fair |
| 5N | 2 | Very poor | Fair |
| 7N | 2 | Poor | Fair |
| 8N | 2 | Poor | Fair |
| 1S | 3 | Poor | Fair |
| 3S | 3 | Very poor | Poor |
| 4S | 3 | Poor | Fair |
| 6S | 3 | Poor | Fair |
| 2S | 4 | Very poor | Fair |
| 5S | 4 | Very poor | Poor |
| 7S | 4 | Very poor | Poor |
| 8S | 4 | Very poor | Poor |

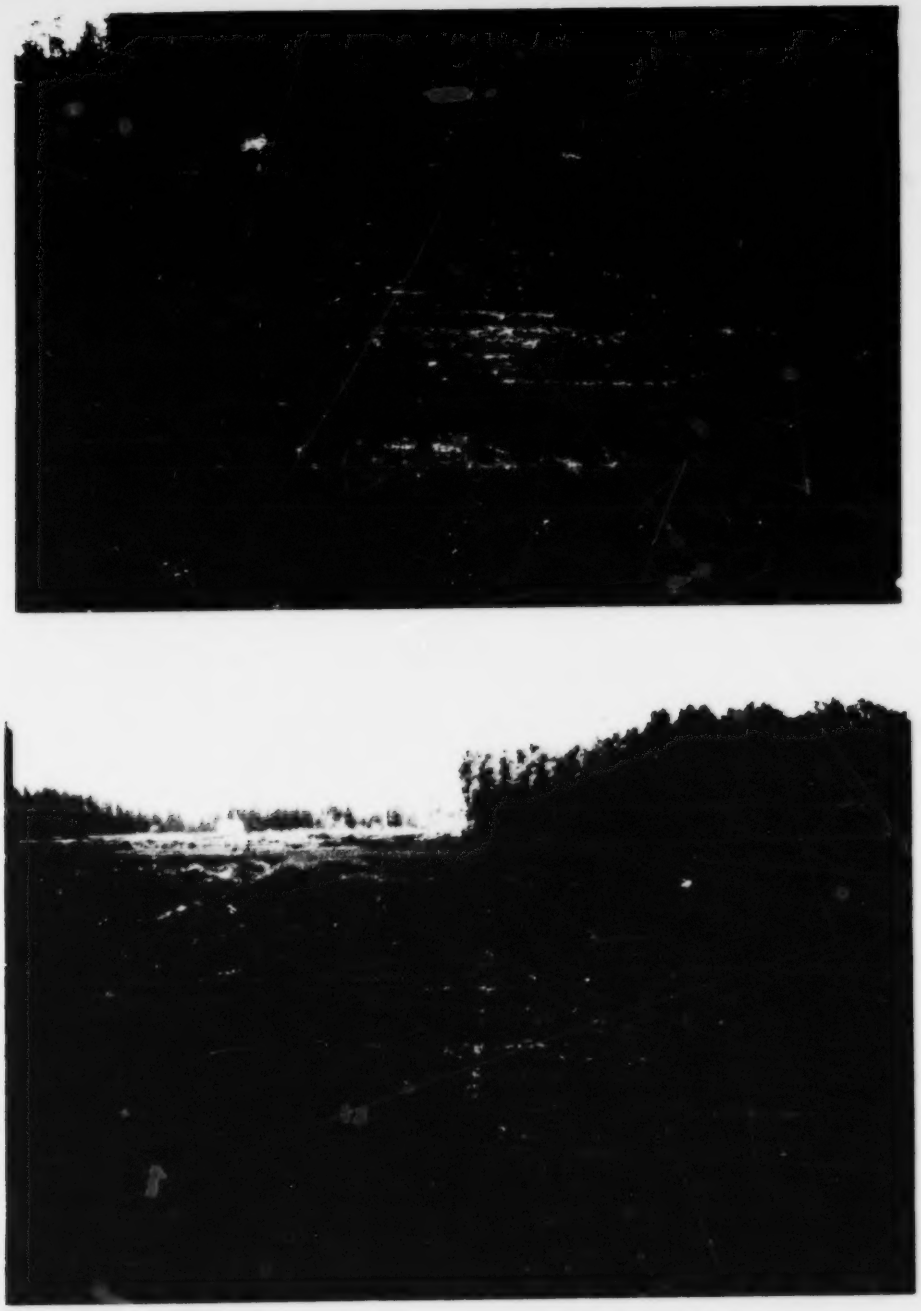

Figure 4. Growth of alfalfa and timothy on Grande Prairie plot 1N (top, sludge loading factor 1) and 8N (bottom, sludge loading factor 2) after one growing season (1986).

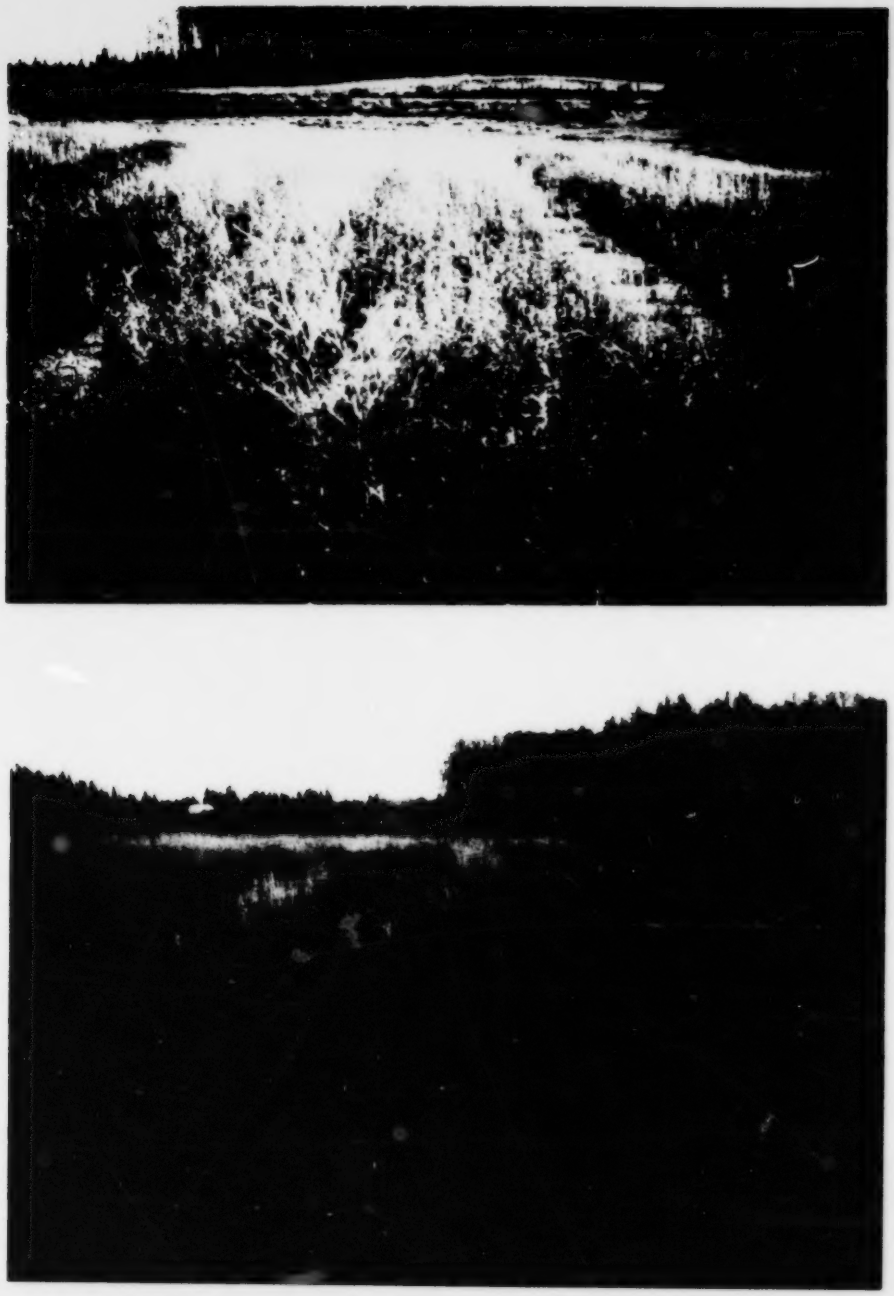

Figure 5. Growth of alfalfa and timothy on Grande Prairie plot 1N (top, sludge loading factor 1) and 8N (bottom, sludge loading factor 2) after two growing seasons (1986 and 1987).

# 6. RESULTS - DRAYTON VALLEY

## 6.1 APPLICATION/DEGRADATION PHASE 1982-1984

### 6.1.1 Oily Sludge Degradation

The initial oil sludge applications at Drayton Valley were the highest of any of the four sites and only one additional application was made to half the plots (Table 12). Although the initial concentrations of oil were 10 and 13.5% in the two sludge treatments, 50% of the oil had disappeared by October of the same year (Figure 6). No detectable degradation occurred between October and May of the following year when an additional application of oil was made to half the plots. In the plots receiving only one application of sludge, 26% of the remaining oil degraded in the second year and 42% in the third year. In the plots with two applications of oil, there was 28% degradation in the second year and 31% in the third year. The overall amount of degradation at Drayton Valley was 75% over the 3 year term of the study with similar rates occurring regardless of the quantities of sludge applied (Table 13).

### 6.1.2 Groundwater and Surface Water Quality

The groundwater from the well showed no evidence of contamination by organic compounds (Table 14). The carbon fractions were variable with time but showed no indications of increases over the 3 year period. There may have been some groundwater contamination with chlorides but it was not excessive. Nitrates increased in the groundwater after 3 years, almost certainly originating from the fertilizer applied to the plots.

The surface water increased in total carbon from 87 mg $L^{-1}$ prior to sludge application to levels between 170 and 223 mg $L^{-1}$ 3 years later. In contrast, chlorides decreased in the runoff pond from about 300 mg $L^{-1}$ soon after sludge application to about 60 mg $L^{-1}$ in the same period. Nitrates increased from 0.1 mg $L^{-1}$ in 1982 to between 2 and 10 mg $L^{-1}$ in 1984.

Table 12. Drayton Valley land treatment plots: summary of oily sludge applications, cultivation and fertilizer treatments.

| Plot | Year sludge added | Sludge added yearly and total, $m^3$ | Sludge loading factor | Rate of: Fertilizer[1] | Rate of: Cultivation[2] |
|---|---|---|---|---|---|
| 1N | 82 | 12.5 | 2 | High | High |
| 1S | 82,83 | 12.5 + 6.2 = 18.7 | 4 | High | High |
| 2N | 82 | 6.2 | 1 | Low | Low |
| 2S | 82,83 | 6.2 + 3.1 = 9.3 | 3 | Low | Low |
| 3N | 82 | 6.2 | 1 | High | Low |
| 3S | 82,83 | 6.2 + 3.1 = 9.3 | 3 | High | Low |
| 4N | 82 | 12.5 | 2 | High | Low |
| 4S | 82,83 | 12.5 + 6.2 = 18.7 | 4 | High | Low |
| 5N | 82 | 6.2 | 1 | Low | High |
| 5S | 82,83 | 6.2 + 3.1 = 9.3 | 3 | Low | High |
| 6N | 82 | 12.5 | 2 | Low | Low |
| 6S | 82,83 | 12.5 + 6.2 = 18.7 | 4 | Low | Low |
| 7N | 82 | 12.5 | 2 | Low | High |
| 7S | 82,83 | 12.5 + 6.2 = 18.7 | 4 | Low | High |
| 8N | 82 | 6.2 | 1 | High | High |
| 8S | 82,83 | 6.2 + 3.1 = 9.3 | 3 | High | High |

[1] Low = 230 kg N $ha^{-1}$ in 1982, 1983 and 1984.

High = 460 kg N $ha^{-1}$ in 1982 and 1983, 230 kg N $ha^{-1}$ in 1984.

[2] High = Rototilling every 2 weeks in 1982 and 1983, every 4 weeks in 1984.

Low = Rototilling every 4 weeks in 1982, 1983 and 1984.

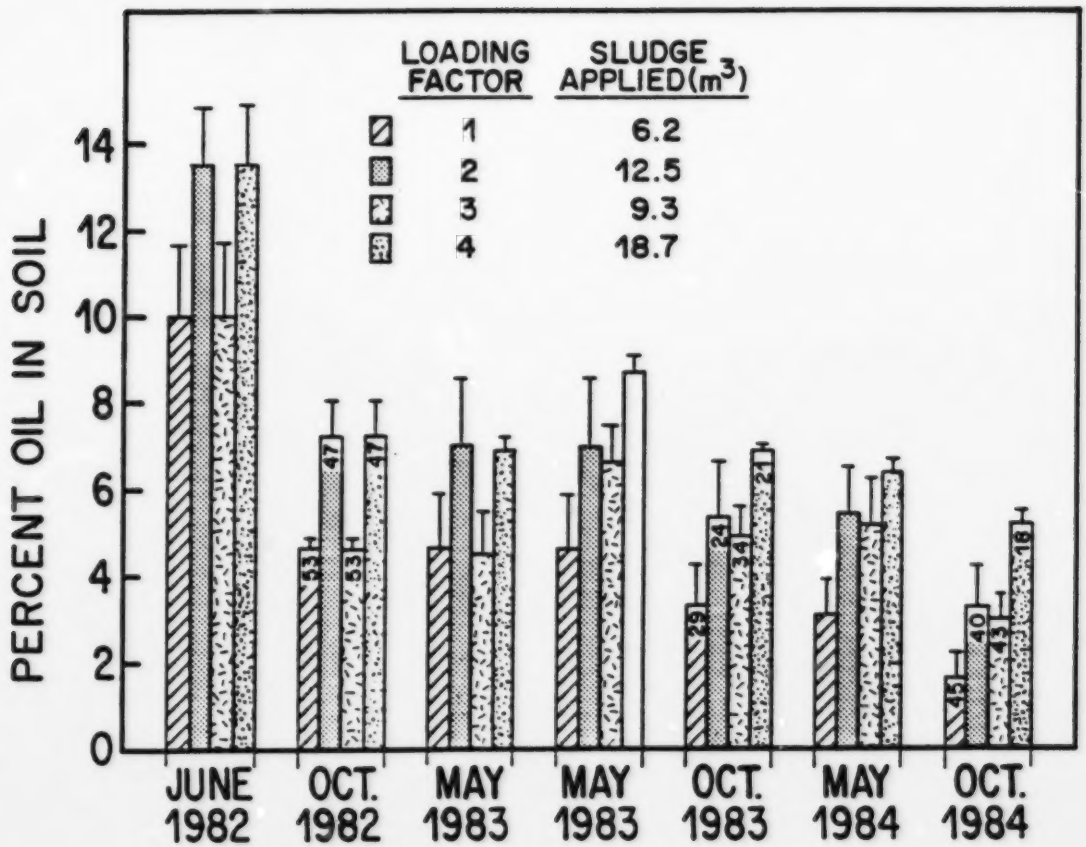


Figure 6. Oil content of soil at Drayton Valley with oil being added to all plots in 1982 and 1984 and to half the plots in 1983. Error bars are S.D., n = 4. Numbers in October bars are percent degradation from preceeding May.

Table 13. Amount of oil applied as sludge to the Drayton Valley land treatment site and subsequent degradation.

| | Loading 3 and 4 | | Loading 1 and 2 | |
|---|---|---|---|---|
| | Oil added and degraded per year (kg $ha^{-1}$) | Percent oil in soil | Oil added and degraded per year (kg $ha^{-1}$) | Percent oil in soil |
| Oil added 1982 | +260,000 | 11.8 | +260,000 | 11.8 |
| Oil degraded 1982/83 | -136,000 | | -131,000 | |
| Oil remaining May 1983 | 124,000 | 5.6 | 129,000 | 5.9 |
| Oil added 1983 | + 46,000 | | 0 | |
| Oil present May 1983 | 170,000 | 7.7 | 129,000 | 5.9 |
| Oil degraded 1983/84 | - 43,000 | | - 34,000 | |
| Oil remaining May 1984 | 127,000 | 5.8 | 95,000 | 4.3 |
| Oil added 1984 | 0 | | 0 | |
| Oil present May 1984 | 127,000 | | 95,000 | |
| Oil degraded 1984 | - 37,000 | | - 39,000 | |
| Oil remaining Oct. 1984 | 90,000 | 4.1 | 55,000 | 2.5 |
| Total oil added | +306,000 | | +260,000 | |
| Total oil degraded | -216,000 | | -205,000 | |
| Overall degradation | 71% | | 79% | |

6.1.3 Contaminant Migration in the Solum

Greater than 90% of the oil was in the upper 15 cm of the soil, with only trace amounts occurring below 30 cm (Table 15). Chlorides were extracted in greater concentrations from samples between 30 and 150 cm than from the surface 30 cm of soil whereas nitrate concentrations were not elevated above those in the control soil.

Table 14. Characteristics of groundwater at Drayton Valley taken from beneath oily sludge treated plots.

| Sample Date | Total Carbon | Volatile Carbon | Organic Carbon | Cl | $NO_3$ | $SO_4$ | pH |
|---|---|---|---|---|---|---|---|
| | | | $mg \cdot L^{-1}$ | | | | |
| June 1982 | 147 | 22 | 52 | 33 | <0.1 | 73 | 7.1 |
| July 1982 | 99 | 8 | 24 | 28 | 1.6 | 64 | 7.1 |
| November 1982 | 107 | 6 | 16 | 58 | <0.1 | 59 | 7.2 |
| June 1983 | 112 | 16 | 23 | 48 | <0.1 | 47 | 8.2 |
| October 1983 | 150 | 34 | 48 | 110 | 3.2 | 77 | 7.6 |
| June 1984 | 128 | 16 | 35 | 56 | 5.3 | 50 | 8.0 |
| October 1984 | 128 | 15 | 40 | 73 | 36.2 | 80 | 8.1 |

Table 15. Concentrations of oil, Cl and $NO_3$ in 1984 in soil treated with oily sludge or in untreated soil at Drayton Valley.

| Depth (cm) | % Oil | | Cl $mg\ L^{-1}$ | | $NO_3$ $mg\ L^{-1}$ | |
|---|---|---|---|---|---|---|
| | Plots | Control | Plots | Control | Plots | Control |
| 0 - 15 | 6.19 | 0.05 | 5 | 7 | <1 | 2 |
| 15 - 30 | 0.56 | 0.02 | 9 | 8 | 6 | 2 |
| 30 - 60 | 0.04 | 0.01 | 31 | 2 | 5 | 2 |
| 60 - 90 | 0.02 | 0.02 | 27 | 4 | 2 | 2 |
| 90 - 120 | 0.02 | 0.02 | 19 | 1 | 2 | 1 |
| 120 - 150 | 0.02 | 0.02 | 21 | 1 | 2 | 2 |

### 6.1.4 Soil Inorganic Chemistry

The soil pH remained above 7 for the duration of the study and generally was between 7.0 and 8.3, although immediately after sludge application the pH was as high as 10.3. The surface soil of heavily treated plots had an SAR of 1.7 in October 1983 and an Ec of 4.1 dS $m^{-1}$. Heavy metal levels were increased by sludge application (Table 16).

## 6.2 DEGRADATION/RECLAMATION PHASE 1986-1987

### 6.2.1 Plant Growth

Four species were seeded in 1986 (see Table 5) but only timothy and red fescue were successful. Small amounts of clover were scattered throughout the area but no foxtail was observed. In the first year growth was good in the plots receiving the least sludge, but was generally poor in plots which received the highest applications (Table 17, Figures 7). In the second year, growth was good in nearly all the plots except those treated with very large amounts of oily sludges (Figure 8). In 1986, inorganic soil chemistry of surface samples from plots of sludge loading levels 1 and 2 indicated that pH, Ec, SAR, extractable cations and anions, and moisture holding capacity did not differ from untreated soil (Danielson et al. 1987).

### 6.2.2 Productivity and Soil Oil Content

Twenty clip plot samples were taken from the loading level 1 and 2 plots (2N, 3N, 4N, 6N) and corresponding soil samples for oil content (no plant samples were available from oil-free soil). With soil oil contents below 2.5% growth of the hay was good (Figure 9, note that two samples with low oil contents were taken from areas not planted properly). Above 3.5% oil, growth was generally poor.

Table 16. Extractable heavy metals in surface soils treated with oily sludges in 1982 and 1983 at Drayton Valley.

| Samples | Cu | Zn | Pb | Cd | Ni |
|---|---|---|---|---|---|
| Pre-application, $\mu g\ g^{-1}$ | 1.8 | 0.4 | 1.6 | 0.04 | 1.8 |
| October 1984, $\mu g\ g^{-1}$ | 7.7 | 58 | 108 | 0.10 | 2.1 |
| Total added, $kg\ ha^{-1}$ | 12 | 115 | 213 | 0.12 | 0.6 |

Table 17. Visual estimates of the growth of timothy-red fescue hay mixture at Drayton Valley in 1986 and 1987.

| Plot | Sludge loading factor | Crop Growth | |
|---|---|---|---|
| | | 1986 | 1987 |
| 2N | 1 | Good | Excellent |
| 3N | 1 | Good | Excellent |
| 5N | 1 | Good | Good |
| 8N | 1 | Good | Good |
| 1N | 2 | Fair | Good |
| 4N | 2 | Fair | Good |
| 6N | 2 | Poor | Fair |
| 7N | 2 | Fair | Fair |
| 2S | 3 | Good | Good |
| 3S | 3 | Good | Good |
| 5S | 3 | Good | Good |
| 8S | 3 | Fair | Fair |
| 1S | 4 | Poor | Fair |
| 4S | 4 | Good | Fair |
| 6S | 4 | Very poor | Poor |
| 7S | 4 | Very poor | Poor |

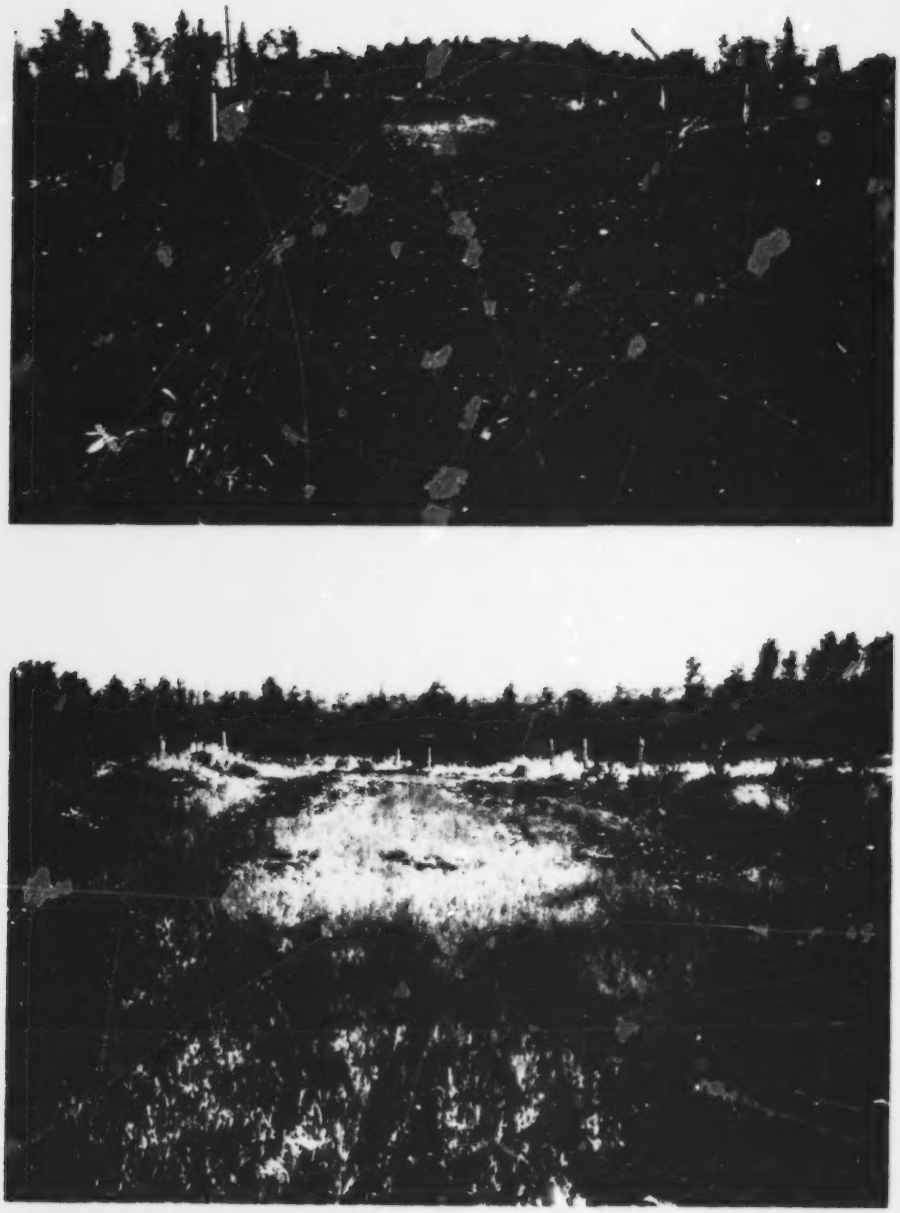

Figure 7. Growth of timothy and red fescue hay on Drayton Valley plots 7S (top, sludge loading factor 4) and 6N (bottom, sludge loading factor 2) after one growing season (1986).

Figure 8. Growth of timothy and red fescue hay on Drayton Valley plots 2S (top, sludge loading factor 2) and 8S (bottom, sludge loading factor 3) after two growing seasons (1986 and 1987).

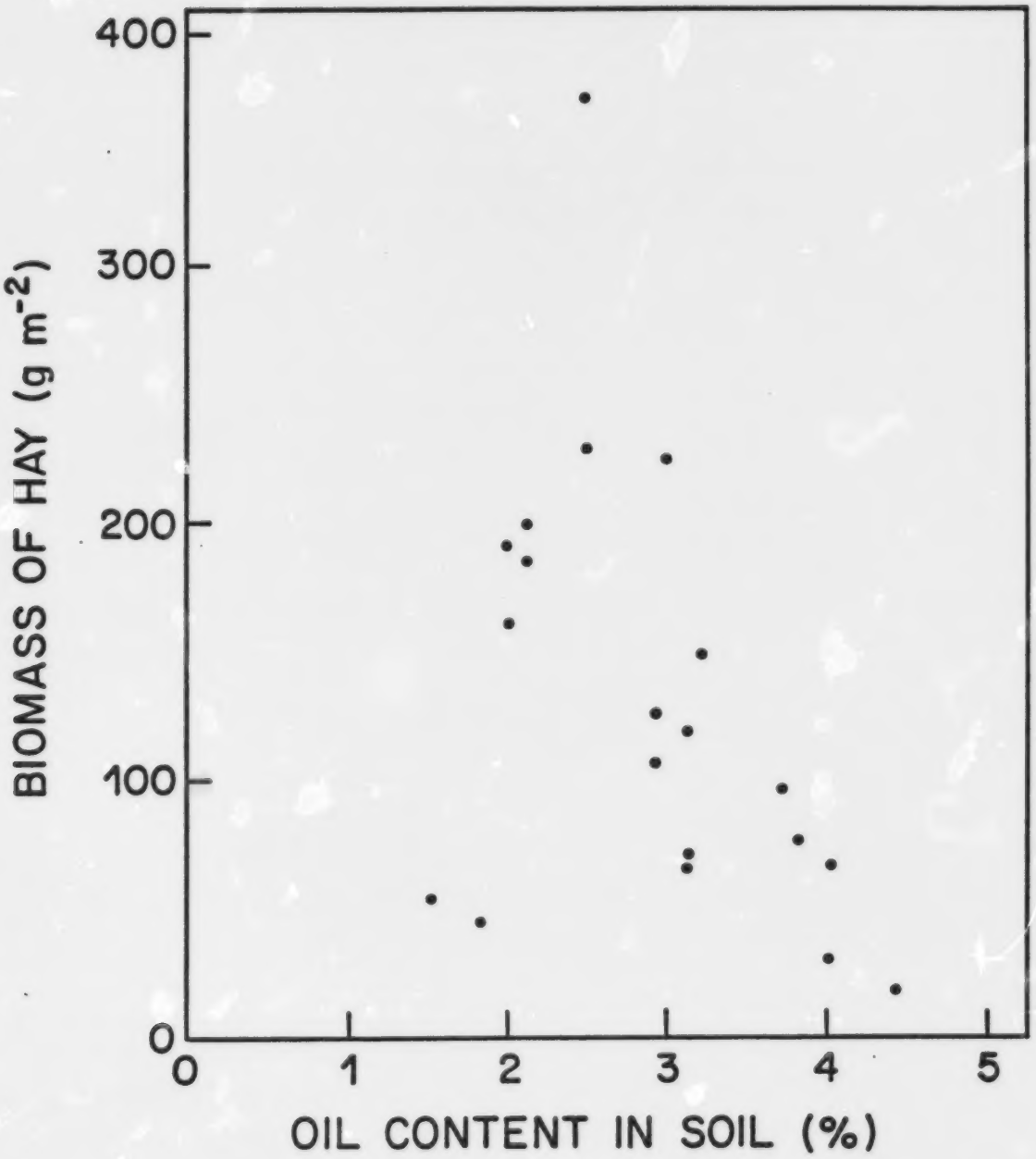


Figure 9. Relationship between soil oil content and hay biomass on clip plots at Drayton Valley after one growing season (1986).

# 7. RESULTS - BROOKS

## 7.1 APPLICATION/DEGRADATION PHASE 1983-1984

### 7.1.1 Oily Sludge Degradation

Studies were of limited intensity on the Brooks site due to the unavoidable delay in initiating the program and the lack of groundwater in the well drilled. Sludge applications were made only twice, in 1983 and 1984 (Table 18). During the first season 18% of the oil disappeared with the heavy application and 27% with the light application (Figure 10). Oil was added to half the plots in 1984 but circumstances prevented further sampling. The total amount of oil added to plots varied by a factor of 2.3 (Table 19).

### 7.1.2 Soil Chemistry

Measurements taken 4 months after sludge application showed soil oil content was 4.55% in the 0 - 15 cm depth, 1.29% in the 15 - 30 cm depth and 0.05% in the 30 - 60 cm depth. The soil pH in 1984 ranged from 7.3 to 8.5. The total amount of heavy metals added with sludge was 1.2 kg $ha^{-1}$ Cu, 25 kg $ha^{-1}$ Zn, 8 kg $ha^{-1}$ Pb, 0.4 kg $ha^{-1}$ Ni and nil amounts of Cd.

## 7.2 DEGRADATION/RECLAMATION PHASE 1986-1988

The plots with sludge loading factors of three and four which received two sludge applications appeared almost barren in 1986 (Table 20, Figure 11). However, upon close inspection, very small plants of both sainfoin and grass were present in all the northern plots. It appeared that the seed had germinated under the moist fall conditions rather than in the droughty spring. In 1987 growth on these plots (loading factors 3 and 4) was still poor with the exception of one plot in which plants had become well-established in 1986. Growth was patchy in all plots (and the control area) but, in general, crested wheatgrass grew well in 1987 in the plots with loading factors of 1 and 2 (Figure 12). It appeared that establishment in 1986 limited coverage and that was determined by microenvironmental moisture conditions coupled with soil oil content stress.

Table 18. Brooks land treatment plots: summary of oily sludge applications, cultivation and fertilizer treatments.

| Plot | Year sludge added | Sludge added yearly and total, $m^3$ | Sludge loading factor | Rate of: Fertilizer[1] | Rate of: Cultivation[2] |
|---|---|---|---|---|---|
| 1S | 83 | 5.6 | 2 | Low | Low |
| 1N | 83, 84 | 5.6 + 2.9 = 8.5 | 4 | Low | Low |
| 2S | 83 | 2.8 | 1 | High | High |
| 2N | 83, 84 | 2.8 + 2.9 = 5.7 | 3 | High | High |
| 3S | 83 | 2.8 | 1 | Low | Low |
| 3N | 83, 84 | 2.8 + 2.9 = 5.7 | 3 | Low | Low |
| 4S | 83 | 5.6 | 2 | Low | High |
| 4N | 83, 84 | 5.6 + 2.9 = 8.5 | 4 | Low | High |
| 5S | 83 | 5.6 | 2 | High | Low |
| 5N | 83, 84 | 5.6 + 2.9 = 8.5 | 4 | High | Low |
| 6S | 83 | 2.8 | 1 | Low | High |
| 6N | 83, 84 | 2.8 + 2.9 = 5.7 | 3 | Low | High |
| 7S | 83 | 5.6 | 2 | High | High |
| 7N | 83, 84 | 5.6 + 2.9 = 8.5 | 4 | High | High |
| 8S | 83 | 2.8 | 1 | High | Low |
| 8N | 83, 84 | 2.8 + 2.9 = 5.7 | 3 | High | Low |

[1] Low = 230 kg N $ha^{-1}$ in 1983 and 1984.
High = 460 kg N $ha^{-1}$ in 1983, 230 kg N $ha^{-1}$ in 1984.

[2] Low = Rototilling every 4 weeks in 1983 and 1984.
High = Rototilling every 2 weeks in 1983 and every 4 weeks in 1984.

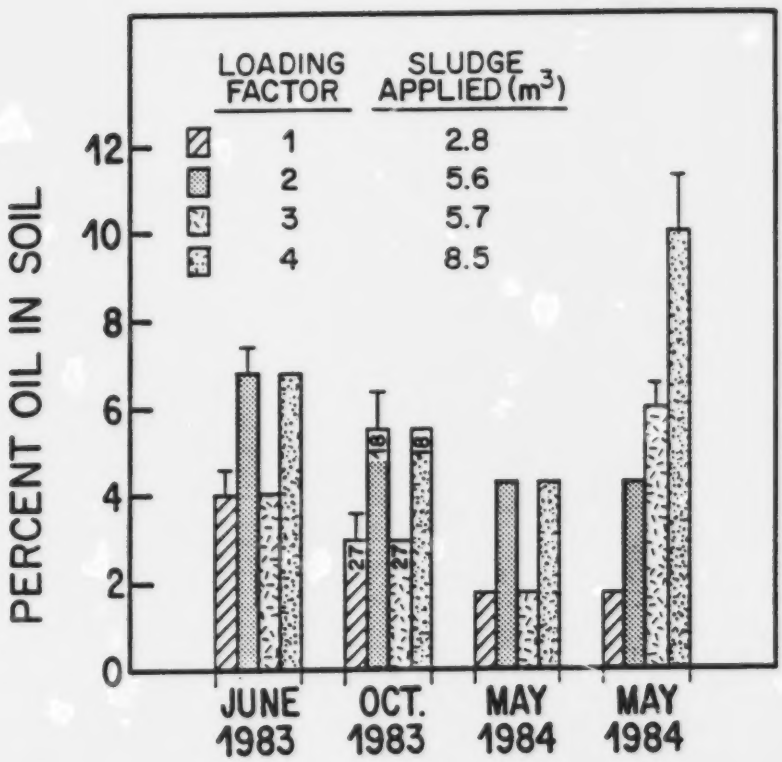


Figure 10. Oil content of soil at Brooks with oil added to all plots in 1983 and to half the plots in 1984. Error bars are S.D., n = 4. Numbers in October bars are percent degradation from preceeding June.

Table 19. Amount of oil applied as sludge to the Brooks land treatment site and subsequent degradation.

| | Loading 3 and 4 | | Loading 1 and 2 | |
|---|---|---|---|---|
| | Oil added and degraded per year (kg $ha^{-1}$) | Percent oil in soil | Oil added and degraded per year (kg $ha^{-1}$) | Percent oil in soil |
| Oil added in 1983 | +122,000 | 5.5 | +122,000 | 5.5 |
| Oil degraded in 1983 | - 42,000 | | - 36,000 | |
| Oil remaining | 80,000 | 3.6 | 86,000 | 3.9 |
| Oil added in 1984 | +117,000 | | 0 | |
| Total oil | 197,000 | 9.0 | 86,000 | 3.9 |

Table 20. Visual estimates of the growth of dryland pasture (primarily crested wheatgrass) on the Brooks land treatment site in 1986 and 1987.

| Plot | Sludge loading factor | Plant Growth | |
|---|---|---|---|
| | | 1986 | 1987 |
| 2S | 1 | Fair | Good |
| 3S | 1 | Fair | Good |
| 6S | 1 | Poor | Good |
| 8S | 1 | Poor | (Weeds) |
| 1S | 2 | Poor | Good |
| 4S | 2 | Poor | Good |
| 5S | 2 | Poor | Good |
| 7S | 2 | Very poor | Fair |
| 2N | 3 | Very poor | Very poor |
| 3N | 3 | Very poor | Good |
| 6N | 3 | Very poor | Poor |
| 8N | 3 | Very poor | (Weeds) |
| 1N | 4 | Very poor | Very poor |
| 4N | 4 | Very poor | Very poor |
| 5N | 4 | Very poor | Very poor |
| 7N | 4 | Very poor | Very poor |

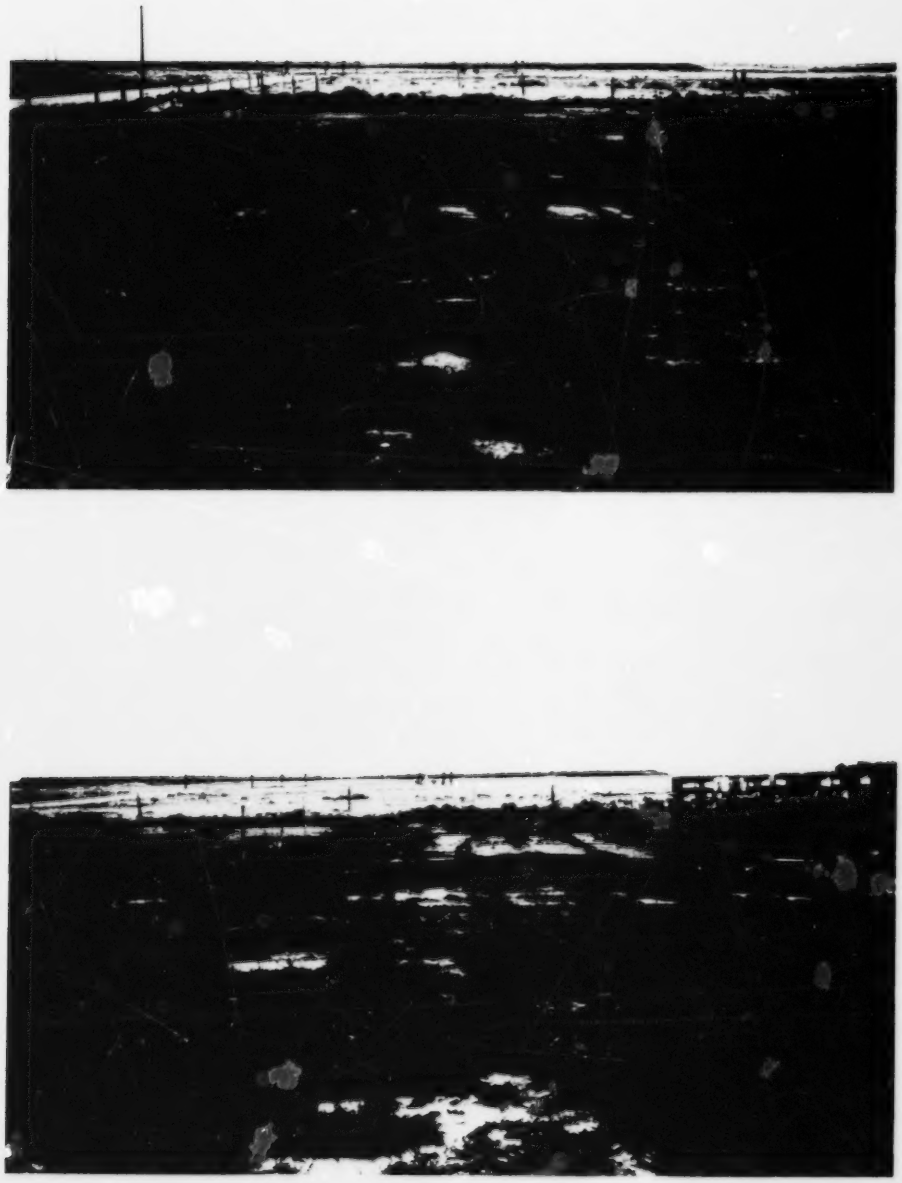

Figure 11. First year growth of dryland pasture at Brooks plot 1S (top, sludge loading factor 2; loading factor 4 in background) and 3S (bottom, sludge loading factor 1, loading factor 3 in background).

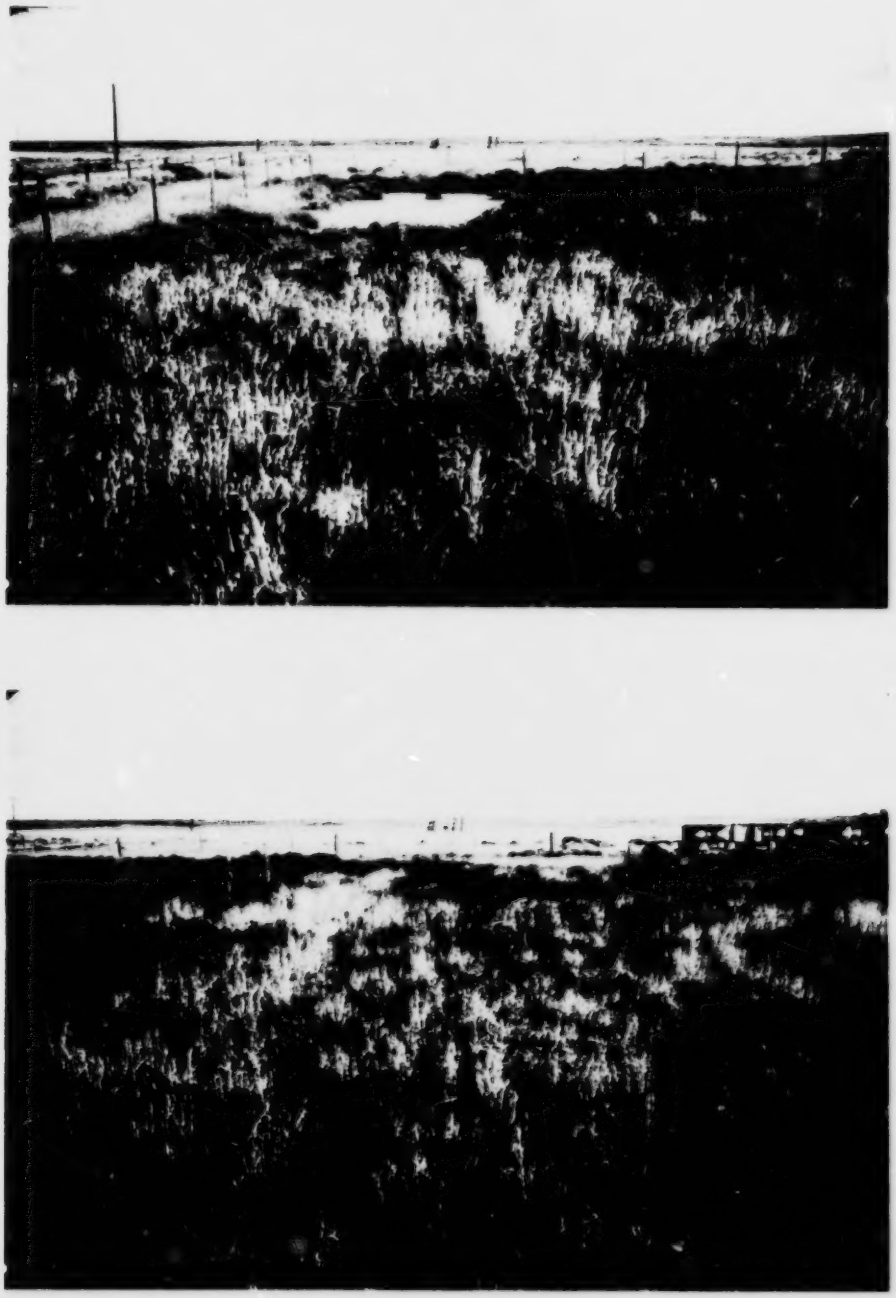

Figure 12. Second year growth (1987) of dryland pasture at Brooks plot 1S (top, sludge loading factor 2, loading factor 4 in background) and 3S (bottom, sludge loading factor 1, loading factor 3 in background).

# 8. RESULTS - LLOYDMINSTER

## 8.1 APPLICATION/DEGRADATION PHASE 1982-1989

### 8.1.1 Oily Sludge Degradation

The Lloydminster site with its heavy oil wastes received the most intense study with detailed attention to groundwater, plant productivity and soil, water and plant risk assessments. Either three or four sludge applications were made to the Lloydminster plots in the 1982 to 1985 period (Table 21). The amount of oil initially added to the plots was relatively small and no degradation in the first year was detected at the low rate and 28% degradation at the high rate (Figure 13). Additional oily sludge was added to half the plots in 1983 and slop oil was added to all the plots in 1984 and 1985.

In the second year, 30% of the remaining oil degraded in the plots that received no additional oil and about 30% of the old plus new oil degraded in the heavy application plots. In 1984, old plus new oil degraded an average of 20% for all four application treatments. After the 1985 slop oil additions, average oil contents ranged from 4.8 to 9.2% and 15% of the oil degraded in the low treatment plots and 24% in the high treatment plots for an overall average of 19% degradation.

In 1986 changes were made in soil processing and as a result there appeared to be no changes in soil oil contents between 1985 and 1986. However, the overall degradation rates were 15% in 1987, 23% in 1988, and 10% in 1989. There was no clear indication that a high soil oil content either favored or inhibited degradation rates as compared to soils containing low levels of oil. However, in Phase 1 of the study, the overall rate of degradation was highest in the plots receiving four sludge applications as compared to those receiving three applications (Table 22). As a result, nearly three times as much oil was degraded in the high treatment plots as in the low treatment plots. By the end of 1989 average oil contents in the four sludge treatments ranged from 2.6 to 3.7%.

Table 21. Lloydminster land treatment plots: summary of oily sludge applications, cultivation and fertilizer treatments.

| Plot | Year sludge added | Sludge added yearly and total, $m^3$ | Sludge loading factor | Rate of: Fertilizer[1] | Rate of: Cultivation[2] |
|---|---|---|---|---|---|
| 1W | 82,84,85 | 4.2 + 1.6 + 2.3 = 8.1 | 1 | Low | Low |
| 1E | 82,83,84,85 | 4.2 + 5.7 + 1.6 + 2.3 = 13.8 | 3 | Low | Low |
| 2W | 82,84,85 | 8.4 + 1.6 + 2.3 = 12.3 | 2 | High | High |
| 2E | 82,83,84,85 | 8.4 + 11.4 + 1.6 + 2.3 = 23.7 | 4 | High | High |
| 3W | 82,84,85 | 8.4 + 1.6 + 2.3 = 12.3 | 2 | Low | High |
| 3E | 82,83,84,85 | 8.4 + 11.4 + 1.6 + 2.3 = 23.7 | 4 | Low | High |
| 4W | 82,84,85 | 4.2 + 1.6 + 2.3 = 8.1 | 1 | High | Low |
| 4E | 82,83,84,85 | 4.2 + 5.7 + 1.6 + 2.3 = 13.8 | 3 | High | Low |
| 5W | 82,84,85 | 8.4 + 1.6 + 2.3 = 12.3 | 2 | Low | Low |
| 5E | 82,83,84,85 | 8.4 + 11.4 + 1.6 + 2.3 = 23.7 | 4 | Low | Low |
| 6W | 82,84,85 | 4.2 + 1.6 + 2.3 = 8.1 | 1 | High | High |
| 6E | 82,83,84,85 | 4.2 + 5.7 + 1.6 + 2.3 = 13.8 | 3 | High | High |
| 7W | 82,84.85 | 4.2 + 1.6 + 2.3 = 8.1 | 1 | Low | High |
| 7E | 82,83,84,85 | 4.2 + 5.7 + 1.6 + 2.3 = 13.8 | 3 | Low | High |
| 8W | 82,84,85 | 8.4 + 1.6 + 2.3 = 12.3 | 2 | High | Low |
| 8E | 82,83,84,85 | 8.4 + 11.4 + 1.6 + 2.3 = 23.7 | 4 | High | Low |

[1] Low = 230 kg N $ha^{-1}$ in 1982, 1983, 1984 and 1985.
High = 460 kg N $ha^{-1}$ in 1982 and 1983, 230 kg N $ha^{-1}$ in 1984 and 1985.

[2] High = Rototilling every 2 weeks in 1982 and 1983, every 4 weeks in 1984 and every 6 weeks in 1985.
Low = Rototilling every 4 weeks in 1982 and 1983, every 4 weeks in 1984 and every 6 weeks in 1985.

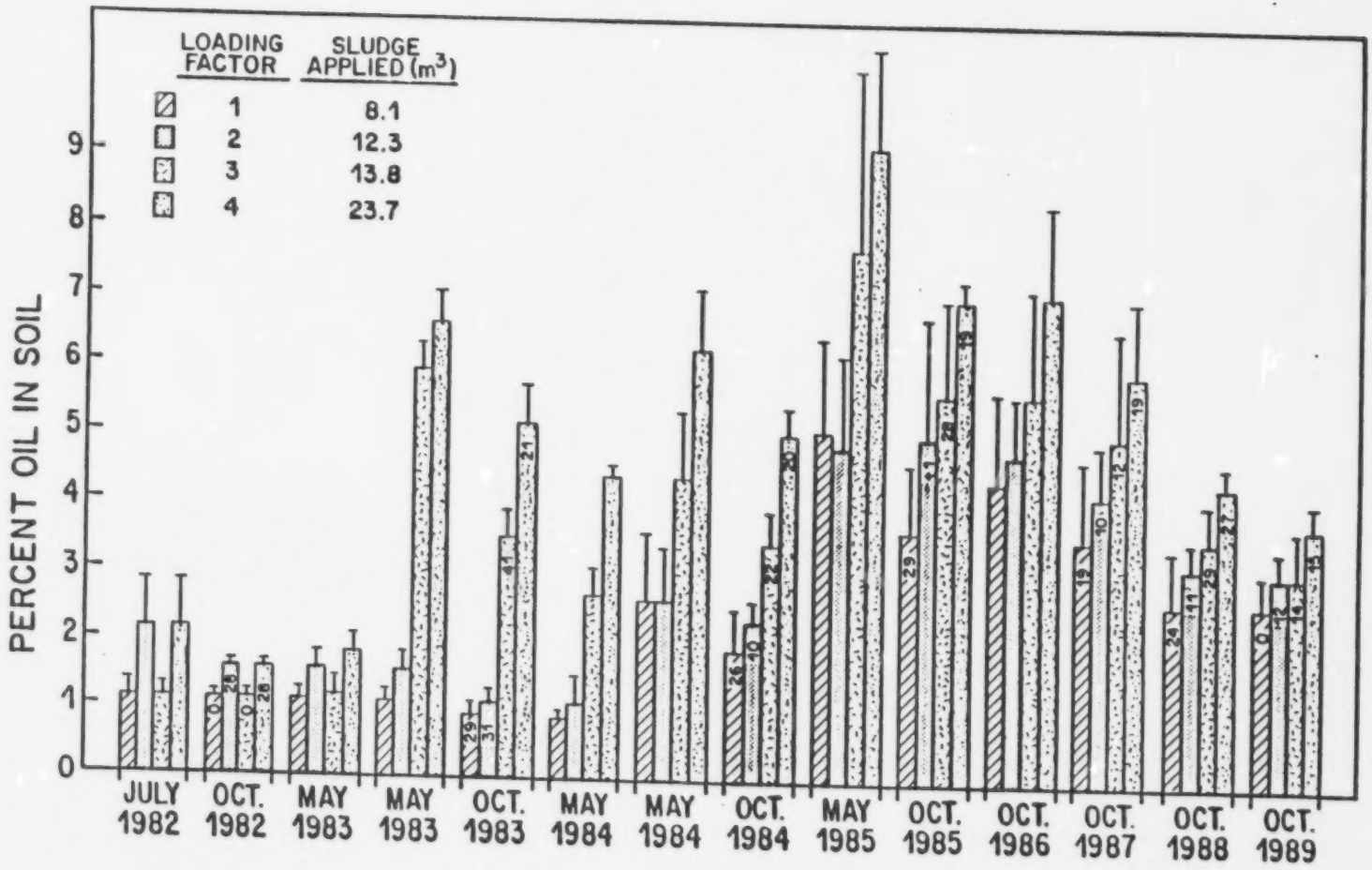


Figure 13. Oil content of soil at Lloydminster with oil added to all plots in 1982, 1984 and 1985 and to half the plots in 1983. Error bars are S.D., n = 4. Numbers in October bars are percent degradation from preceeding May (1982-1985) or October 1987-1989).

Table 22. Amounts of oil applied as sludge and slop oil to the Lloydminster land treatment site and subsequent degradation in 1982 to 1985.

| | Loading 3 and 4 | | Loading 1 and 2 | |
|---|---|---|---|---|
| | Oil added and degraded per year (kg $ha^{-1}$) | Percent oil in soil | Oil added and degraded per year (kg $ha^{-1}$) | Percent oil in soil |
| Oil added in 1982 | +37,000 | 1.7 | +37,000 | 1.7 |
| Oil degraded in 1982 | -4,000 | | -6,000 | |
| Oil remaining | 33,000 | 1.5 | 31,000 | 1.4 |
| Oil added in 1983 | +104,000 | | 0 | |
| Total oil present | 137,000 | 6.2 | 31,000 | 1.4 |
| Oil degraded in 1983 | -59,000 | | -10,000 | |
| Oil remaining | 78,000 | 3.6 | 21,000 | 1.0 |
| Oil added in 1984 | +38,000 | | +36,000 | |
| Total oil present | 116,000 | 5.3 | 57,000 | 2.6 |
| Oil degraded in 1984 | -24,000 | | -10,000 | |
| Oil remaining | 92,000 | 4.2 | 47,000 | 2.1 |
| Oil added in 1985 | +90,000 | | +67,000 | |
| Total oil present | 182,000 | 8.3 | 114,000 | 5.2 |
| Oil degraded in 1984 | -43,000 | | -19,000 | |
| Oil remaining | 139,000 | 6.3 | 95,000 | 4.3 |
| Total oil added | +269,000 | | +140,000 | |
| Total oil degraded | -130,000 | | -45,000 | |
| Overall degradation | 48% | | 32% | |

### 8.1.2 Asphaltene Degradation

The amount of asphaltenes in oil extracted from the soil in 1982 was 19.8%, and the amount of asphaltenes in oil extracted from the heavily treated plots in 1985 was 18.7%. In the second phase of the study, asphaltenes were measured in all the plots. There was a steady decrease in the quantity of asphaltenes in the soil with time with overall averages for 1986, 1987, 1988 and 1989 of 1.03, 0.91, 0.77 and 0.64%, respectively (Figure 14). Over the 3 year period, 36% of the asphaltenes were biodegraded when all treatments were averaged together.

There was no apparent trend for the proportion of the extracted oil composed of asphaltenes to increase with time (Figure 15). For all 16 plots the average asphaltene content of the oil was 18.9% in 1986, 19.5% in 1987, 22.7% in 1988 and 20.4% in 1989.

### 8.1.3 Inorganic and Organic Contaminant Migration in the Solum

Four years after the first application of oily sludge to the plots only trace amounts of oil were present below 30 cm and 78% of the residual oil was in the upper 15 cm of soil (Table 23). Chlorides had contaminated the soil more or less uniformly to at least a depth of 1.5 m and nitrates were contaminating the subsoil but nitrate levels were low in the cultivated root zone.

In 1989 oil contents had decreased and there was no evidence that oil was being transported down the soil profile. Chloride concentrations, electrical conductivity and SAR values were all moderate in the root zone (Table 24). Nitrates occurred at higher concentrations in the subsurface soil than in the layer containing roots and residual oil.

The surface 45 cm of soil of a plot heavily treated with oily sludge was analysed for the presence of potentially toxic aromatic compounds in 1989. Oil was extracted from root zone soil and the subsoil to determine if specific aromatic compounds were present and if present, to determine if they were migrating down the profile and could thus represent future groundwater contaminants.

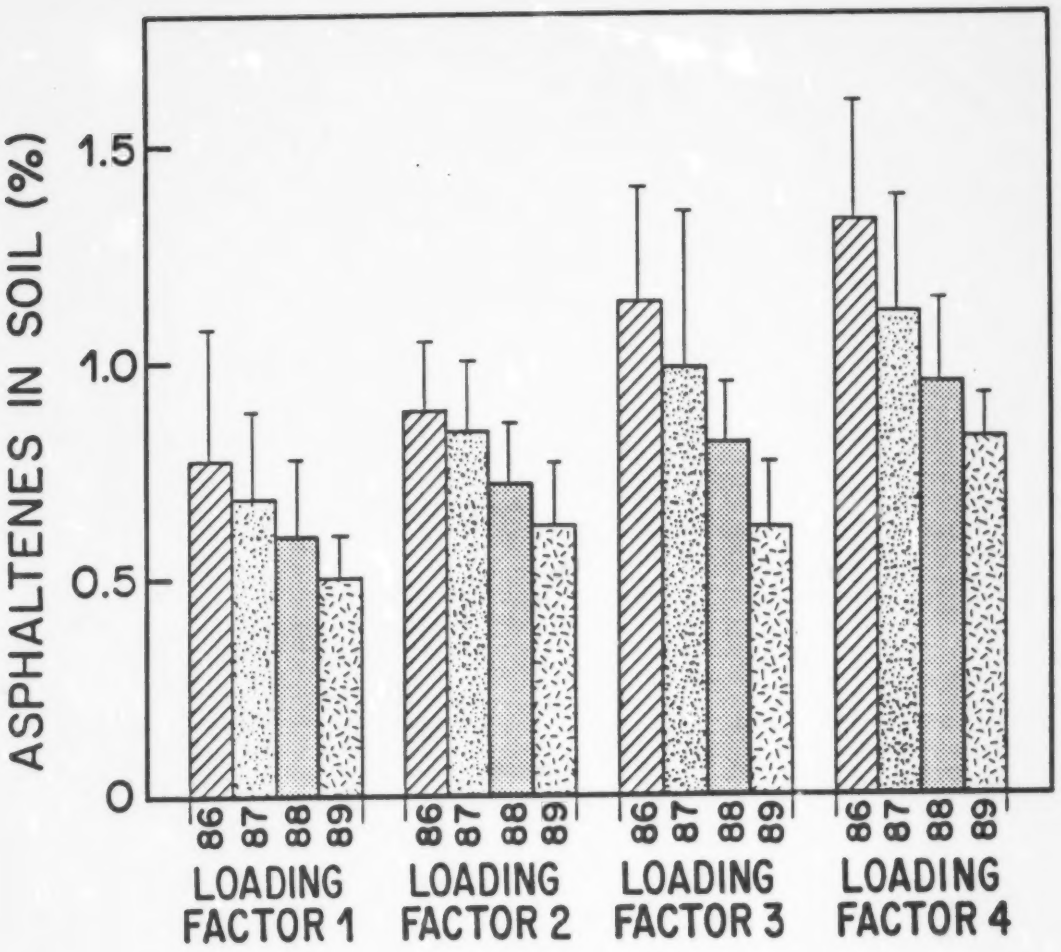


Figure 14. Asphaltene content in 1986 to 1989 of soil at Lloydminster which was treated with oily wastes 1982 to 1985 inclusively. Sludge loading factors are relative rates of oil application (1 = low, 4 = high). Error bars are S.D., n = 4.

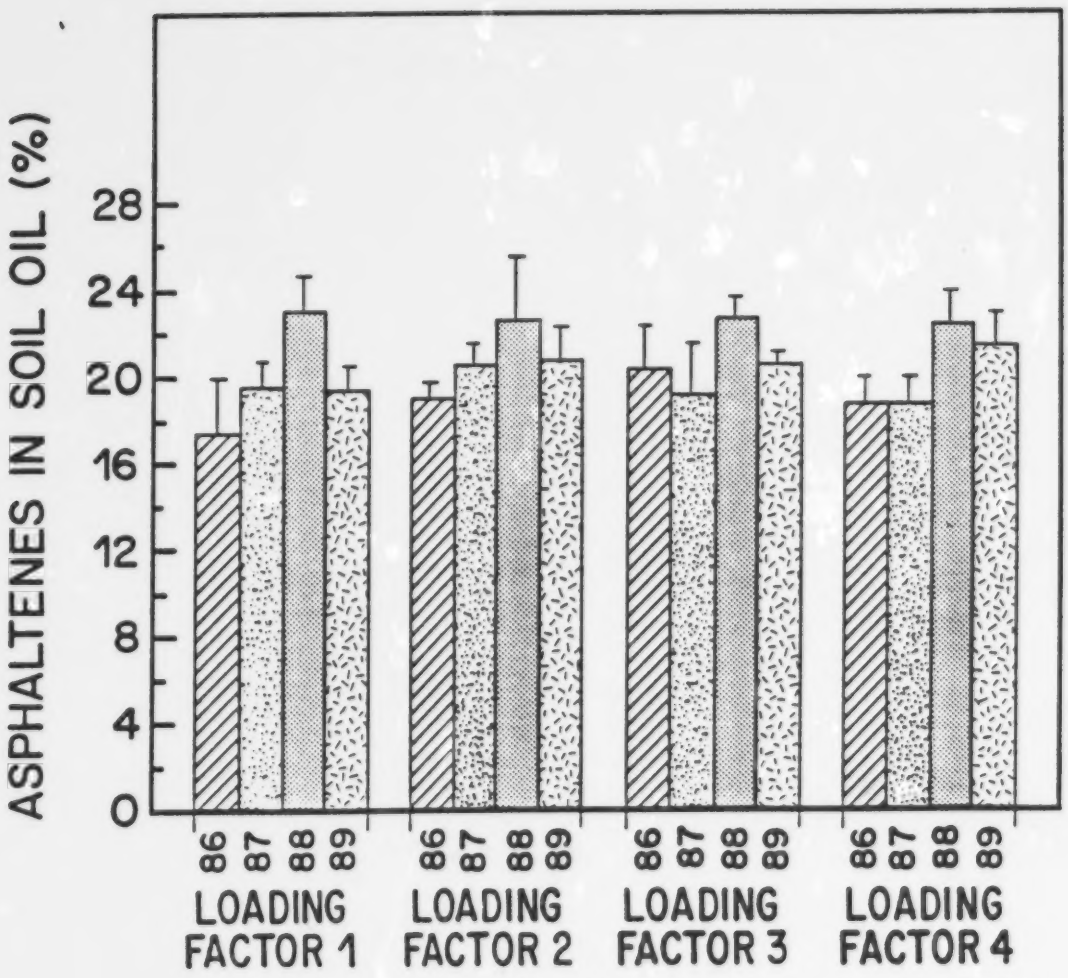


Figure 15. Percentage of oil composed of asphaltenes that was extracted from Lloydminster soils treated with oily wastes 1982 to 1985 inclusively and measured in 1986 to 1989. Loading factors indicate relative rates of oil application (1 = low, 4 = high). Error bars are S.D., n = 4.

Table 23. Concentrations of oil, Cl and $NO_3$ in 1985 in soil treated with oily sludge or in untreated soil at Lloydminster.

| Depth (cm) | % Oil | | Cl mg $L^{-1}$ | | $NO_3$ mg $L^{-1}$ | |
|---|---|---|---|---|---|---|
| | Plots | Control | Plots | Control | Plots | Control |
| 0 - 15 | 6.01 | 0.02 | 103 | 4 | 2 | 20 |
| 15 - 30 | 1.64 | 0.02 | 167 | 4 | 4 | 10 |
| 30 - 60 | 0.05 | 0.01 | 73 | 3 | 52 | 9 |
| 60 - 90 | 0.01 | 0.02 | 68 | 2 | 58 | 4 |
| 90 - 120 | 0.01 | 0.01 | 132 | 2 | 19 | 3 |
| 120 - 150 | 0.01 | 0.01 | 116 | 4 | 9 | 3 |

Table 24. Oil content and soil chemistry of soil from two profiles of Lloydminster Plot 8E sampled for possible presence and migration of organic contaminants originating from oily sludges in 1989. Data are means ± SD, n=2.

| Soil Depth cm | Oil Content % | Organic Carbon % | SAR | Ec dS $m^{-1}$ | Cl mEq $L^{-1}$ | $NO_3$ mEq $L^{-1}$ |
|---|---|---|---|---|---|---|
| 0-15 | 4.79 ± 0.42 | 7.3 ± 1.6 | 2.2 ± 0.6 | 2.1 ± 0.4 | 1.9 ± 0.3 | 1.5 ± 2.0 |
| 15-30 | 0.68 ± 0.04 | 3.0 ± 0.2 | 3.3 ± 1.2 | 2.2 ± 0.5 | 2.4 ± 1.5 | 6.2 ± 6.0 |
| 30-45 | 0.02 ± 0 | 0.5 ± 0.1 | 7.1 ± 0.4 | 1.3 ± 0.2 | 2.0 ± 1.1 | 4.4 ± 4.1 |

Prior to the GC/MS analysis of the extracted oils, a standard solution containing each of the target compounds was analyzed to determine gas chromatographic (GC) retention times and detection limits. The target compounds were: (a) dibenzothiophene of molecular weight (mw) 184, (b) pyridine of mw 79, (c) carbazole of mw 167, (d) 2-methylnaphthalene of mw 142, (e) biphenyl of mw 154, (f) acridine of mw 179, (g) 4-methylbiphenyl of mw 168, and (h) 9-ethylfluorene of mw 194. A chromatogram of these standards together with a mixture of deuterated internal standards is shown in Figure 16 (top). The target compounds had GC retention times in the range of 400-2000 seconds.

The chromatograms of the oils extracted from the cores showed no peaks, other than deuterated internal standards, in the 400-2000 second range. An example of the analyses is the surface sample results shown in Figure 16 (bottom). A computerized search for the characteristic masses of the target compounds failed to detect the presence of any of these compounds. The detection limit was 0.003 $\mu g\ g^{-1}$ of soil or 0.060 $\mu g\ g^{-1}$ of oil. It is concluded that the target compounds were not present in the degraded Lloydminster heavy oil.

These results are in keeping with the normal composition of the Lloydminster heavy oil which does not contain these relatively low molecular weight compounds. Furthermore it is unlikely that they would be generated during degradation of higher molecular weight materials under field conditions. With the exception of pyridine, they occur in much lighter oils and because their deuterated analogues can be readily purchased they would be ideal for laboratory-based microbiological degradation studies. These compounds are not suitable for biodegradation studies of heavy oils.

### 8.1.4 Groundwater and Surface Water Quality

In the 1982 to 1985 period there was no evidence that groundwater had been contaminated with organic compounds based on total, volatile, and organic carbon analyses (Table 25). How- ever, both chloride and nitrate concentrations increased abruptly in 1982, indicating either leaks around the well casing or rapid migration through the subsoil. Sulphate concentrations decreased throughout the sampling period.

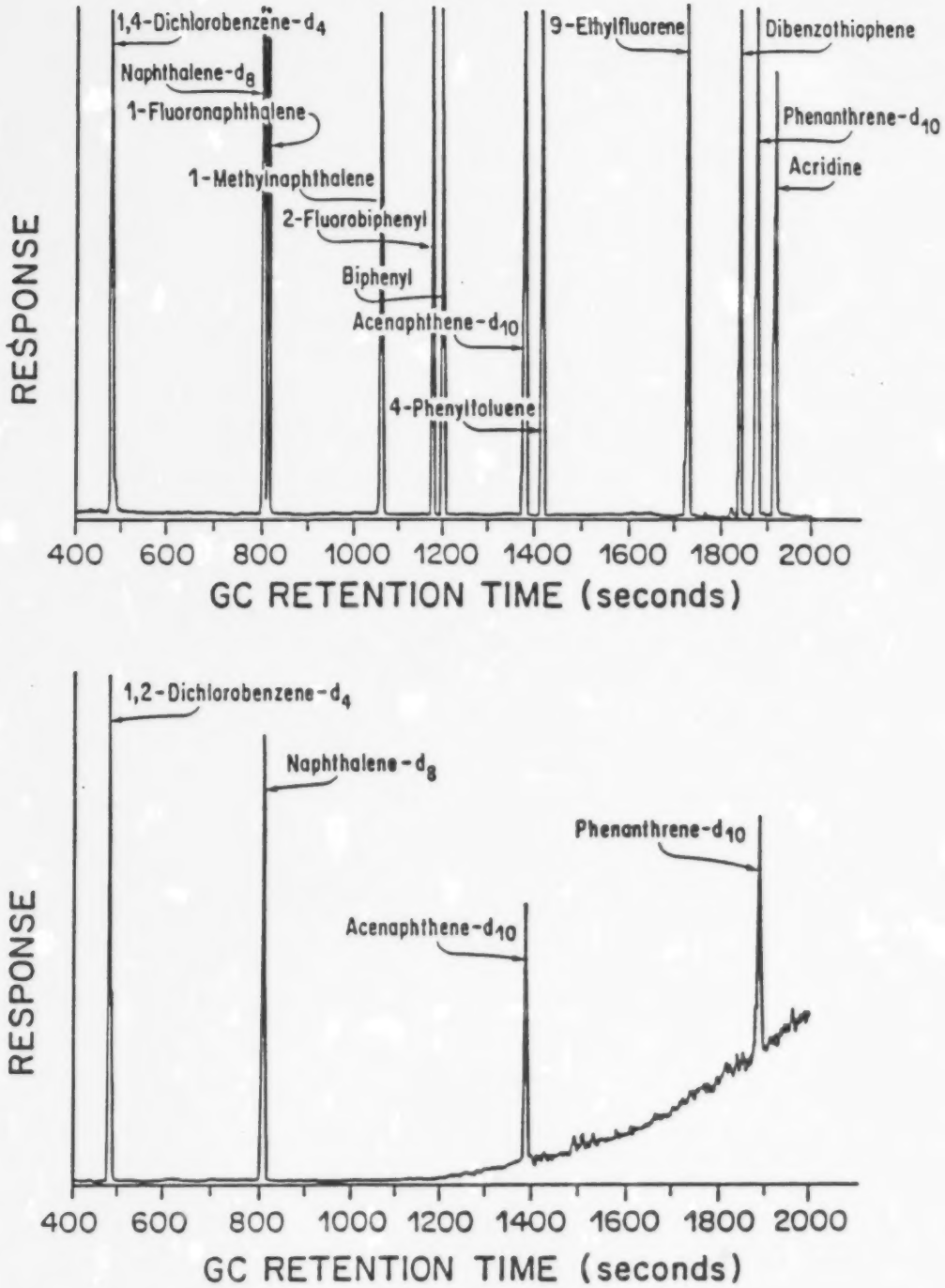


Figure 16. GC-MS total ion chromatograph of target compounds and deuterated standards (top) and of oil from Plot 8E, 0 - 15 cm depth with internal standards (bottom).

8.1.5 Soil Inorganic Chemistry

The soil pH in 1985 ranged from 7.0 to 8.6 with most values between 7.3 and 8.2. Electrical conductivity increased from 0.5 dS $m^{-1}$ prior to treatment to 4.5 dS $m^{-1}$ in 1985. In the same period the SAR increased from 0.2 to 9.2. The concentrations of extractable Cu, Zn and Pb increased due to sludge application but little changes occurred in concentrations of Cd or Ni (Table 26).

8.2 DEGRADATION/RECLAMATION PHASE 1986-1989

8.2.1 Plant Growth

The growth of the initial crop of barley in 1986 ranged from poor to excellent in the sludge treated plots (Table 27, Figure 17). Growth was not strictly related to amount of sludge added although, with one exception, growth was poor on plots that received four sludge applications. The roots of barley plants that were growing poorly were stunted and only appeared to penetrate the surface few centimeters of soil.

Growth in the second year of the Degradation/Reclamation Phase was similar to that in the previous year (Figure 18) or somewhat improved but there was often a high degree of within plot variability. Results for the first 2 years indicated that good growth of crops was possible if oil contents were below 4%, although growth could still be poor if oil contents were in the 2.5 - 4.0% range (Figures 19, 20). In this intermediate range it appeared that salt stress was coupled with oil stress to severely limit growth. In 1987, salt concentrations where growth exceeded 150 g $m^{-2}$ did not exceed 2.9 dS $m^{-1}$ except in one instance. In a transect displaying a gradual change in barley growth from good to poor, salt concentrations were low and the growth effects appeared to be controlled by soil oil content and moderately good growth was possible even with an oil content of 4.9% (Table 28). In both 1986 and 1987, good growth only occurred on soil with low salt concentrations regardless of oil content.

Table 25. Characteristics of groundwater at Lloydminster taken from beneath oily sludge treated plots in 1982 through 1985.

| Sample Date | Total Carbon | Volatile Carbon | Organic Carbon | Cl | $NO_3$ | $SO_4$ | pH |
|---|---|---|---|---|---|---|---|
| | $mg \cdot L^{-1}$ | | | | | | |
| June 1982 | 190 | 53 | 67 | 3 | <0.1 | 2830 | 7.0 |
| August 1982 | 115 | 16 | 37 | 239 | <0.1 | 927 | 7.4 |
| October 1982 | 125 | 19 | 56 | 579 | 41 | 744 | 7.0 |
| June 1983 | 123 | 17 | 30 | 151 | 32 | 934 | 7.3 |
| October 1983 | 166 | 9 | 37 | 103 | 42 | 299 | 7.8 |
| May 1984 | 127 | 6 | 22 | 59 | 45 | 371 | 8.0 |
| October 1984 | 170 | 19 | 52 | 320 | 67 | 123 | 8.0 |
| June 1985 | 119 | 5 | 55 | 784 | 54 | 155 | 7.5 |
| October 1985 | 122 | 8 | 32 | 805 | 84 | 96 | 7.4 |

Table 26. Extractable heavy metals in surface soils treated with oily sludges in 1982, 1984 and 1985 at Lloydminster.

| Samples | | Cu | Zn | Pb | Cd | Ni |
|---|---|---|---|---|---|---|
| Pre-application | $\mu g\ g^{-1}$ | 0.8 | 0.4 | 0.6 | 0.04 | 0.8 |
| October 1984 | $\mu g\ g^{-1}$ | 1.1 | 3.1 | 3.3 | 0.05 | 0.9 |
| Total added | $kg\ ha^{-1}$ | 0.6 | 5.4 | 5.4 | 0.02 | 0.2 |

Table 27. Visual estimates of the growth of barley on the Lloydminster land treatment site.

| Plot | Sludge loading factor | Crop Growth | |
|---|---|---|---|
| | | 1986 | 1987 |
| 1W | 1 | Good | ND |
| 4W | 1 | Fair | Fair-good |
| 6W | 1 | Fair | Fair |
| 7W | 1 | Fair | Poor-fair |
| 2W | 2 | Very poor | ND |
| 3W | 2 | Poor | Fair |
| 5W | 2 | Poor | Poor-fair |
| 8W | 2 | Good | Good |
| 1E | 3 | Good | ND |
| 4E | 3 | Poor | Poor |
| 6E | 3 | Very poor | Poor-fair |
| 7E | 3 | Poor | Poor |
| 2E | 4 | Poor | ND |
| 3E | 4 | Poor | Poor |
| 5E | 4 | Poor | Very poor |
| 8E | 4 | Poor | Very poor |

ND = not determined; crop assessments not possible

Table 28. Soil chemical characteristics of five adjacent 1 m² locations on a transect in which plant growth ranged from poor to good in 1987.

| Barley Yield (g) | Oil Content (%) | Total Carbon (%) | Ec (dS $m^{-1}$) | SAR | Na | Cl | $SO_4$ |
|---|---|---|---|---|---|---|---|
| | | | | | (m.e. $L^{-1}$) | | |
| 41 | 5.0 | 6.4 | 1.7 | 3.1 | 7.8 | 3.0 | 7.1 |
| 113 | 5.9 | 6.8 | 1.6 | 2.5 | 6.5 | 2.0 | 7.1 |
| 246 | 4.9 | 6.6 | 1.4 | 2.3 | 5.5 | 1.5 | 5.9 |
| 269 | 4.1 | 6.3 | 1.2 | 1.8 | 4.3 | 1.4 | 3.9 |
| 523 | 3.8 | 5.8 | 1.3 | 1.8 | 4.4 | 2.1 | 4.3 |

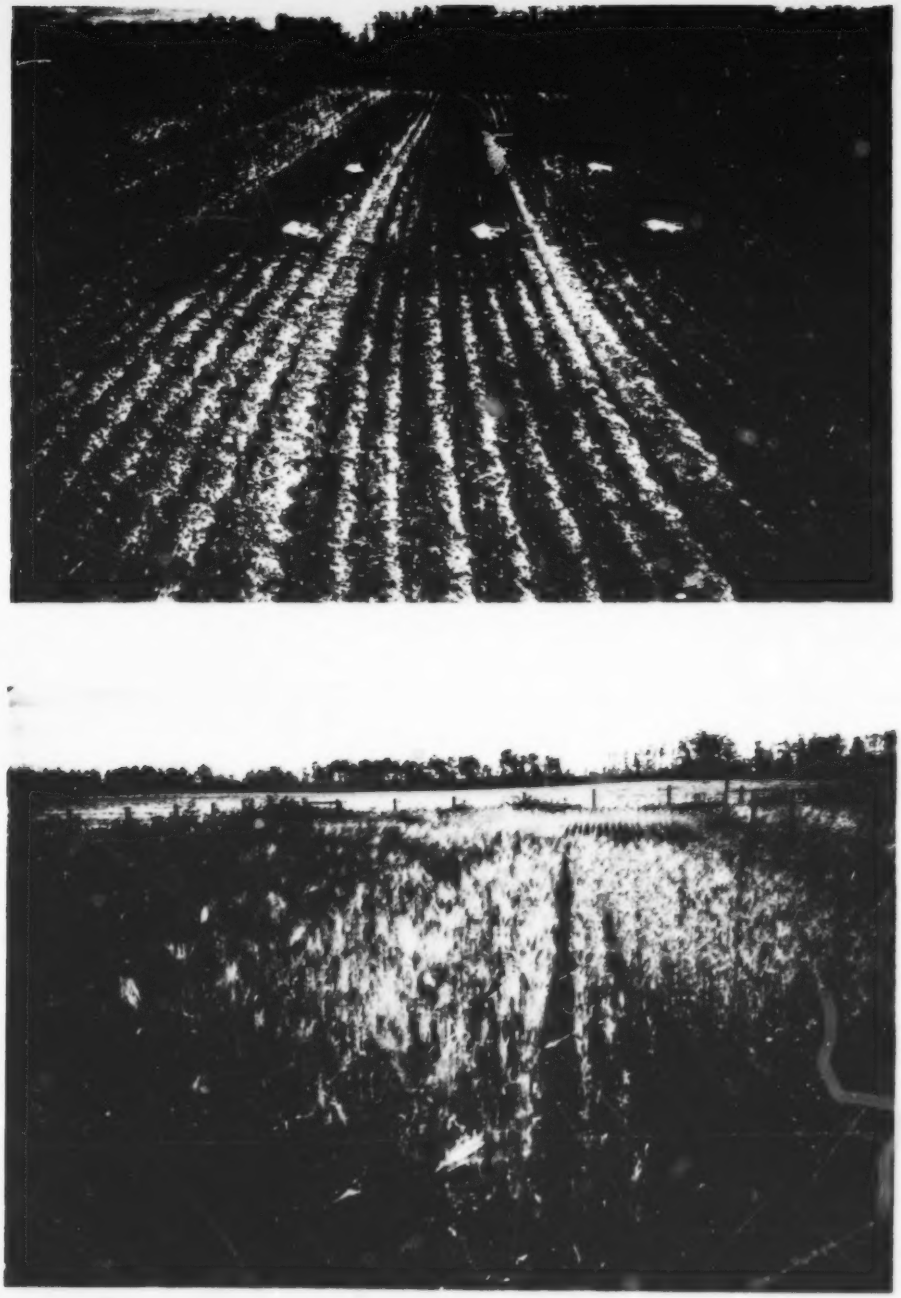

Figure 17. First year (1986) growth of barley on Lloydminster land treatment plot 5W (top, sludge loading factor 2, runoff pond in background) and plot 8W (bottom, sludge loading factor 2).

Figure 18. Second year (1987) growth of barley on Lloydminster land treatment plot 5W (top, sludge loading factor 2) and plot 8W (bottom, sludge loading factor 2).

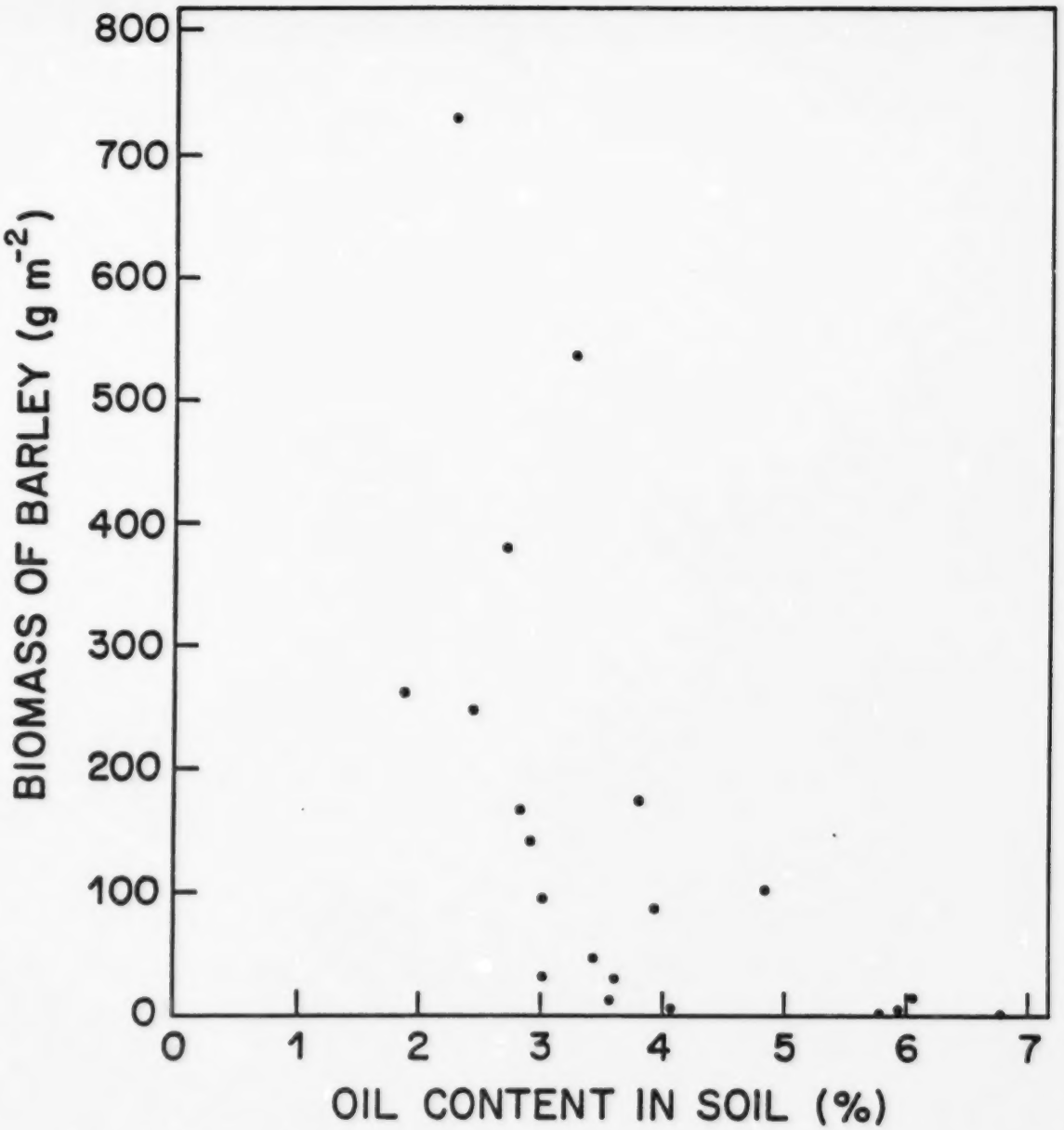


Figure 19. Relationship between soil oil content and barley biomass on clip plots at Lloydminster one year after the last oily sludge application (1986).

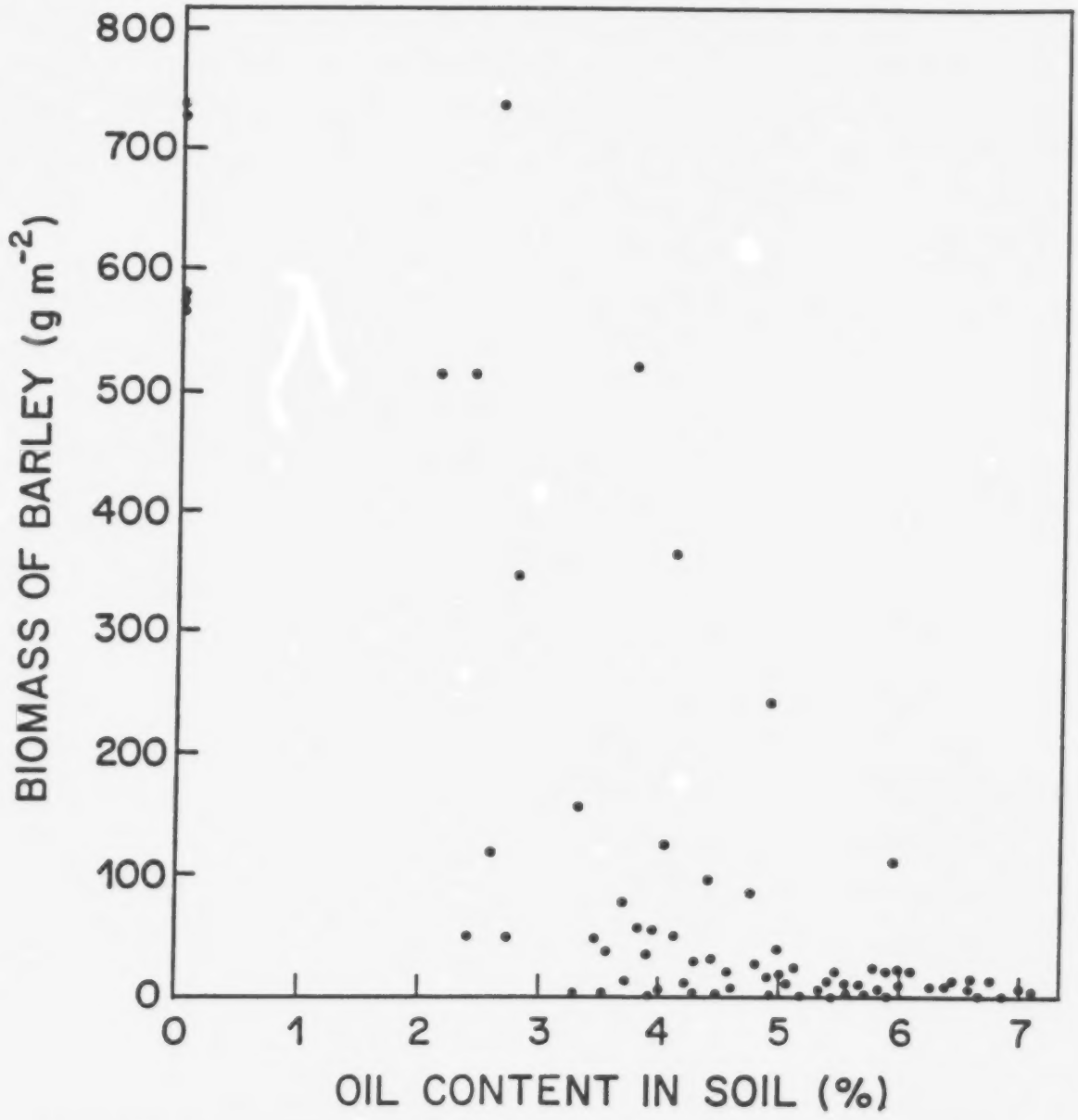


Figure 20. Relationship between soil oil content and barley biomass on clip plots at Lloydminster two years after the last oily sludge application (1987).

As soil conditions for plant growth did not appear to be improving rapidly, means were taken to hasten rehabilitation of the site. These included deep ripping to allow better leaching, heavy nitrogen fertilization to enhance microbial degradation of hydrocarbons, and application of manure as a general soil amendment (see Section 3.4.4). The result of these practices was greatly improved growth of barley in 1988 as compared to the two previous years (Figures 21, 22). In the west plots (loading factors 1 and 2) biomass exceeded 300 g $m^{-2}$ in all eight plots whereas the year previous, yields were as low as 21 g $m^{-2}$. Growth was still poor in some plots that received four sludge applications but growth was improved in every plot when compared to 1987. Growth was 7-fold higher in the plots that were not treated with manure than in the same plots the previous year. Manure improved the growth of barley substantially in all eight plots, yields were 2.4 fold higher on plots receiving manure than on comparable plots that were just deep ripped and fertilized.

Yields of barley in 1988 on all the 125 individual clip plots are compared to the corresponding oil contents in the soil in Figure 23. In 1987 only 7% of 1 $m^2$ plots exceeded biomass production of 300 g $m^{-2}$, but in 1988, 53% of the clip plots exceeded this value. In the range of 3 to 5% oil, yields were extremely variable and below 3% nearly all plots exceeded 50% (382 g) of the average yield in the control field. Above 5% oil content, yields were very poor. The very worst (2 g $m^{-2}$) and very best (915 g $m^{-2}$) clip plots both had the same soil oil content (3.5%). The high variability may be due to differential rates of oil degradation during the growing season as the oil content values were obtained at the end of the growing season.

As the remedial measures taken had been successful, all the plots were deep ripped, fertilized and manured in the fall of 1988 and the area replanted in 1989. Growth of barley in 1989 was very good and nearly uniform in all plots regardless of past sludge treatment history (Figure 24). Barley yields exceeded 400 g $m^{-2}$ in all 80 clip plots and average values ranged from 592 to 792 g $m^{-2}$ in the 16 plots. Control values were not available as the adjacent field was not planted to barley but all the plots compared favorably to previous measurements made on oil-free soil.

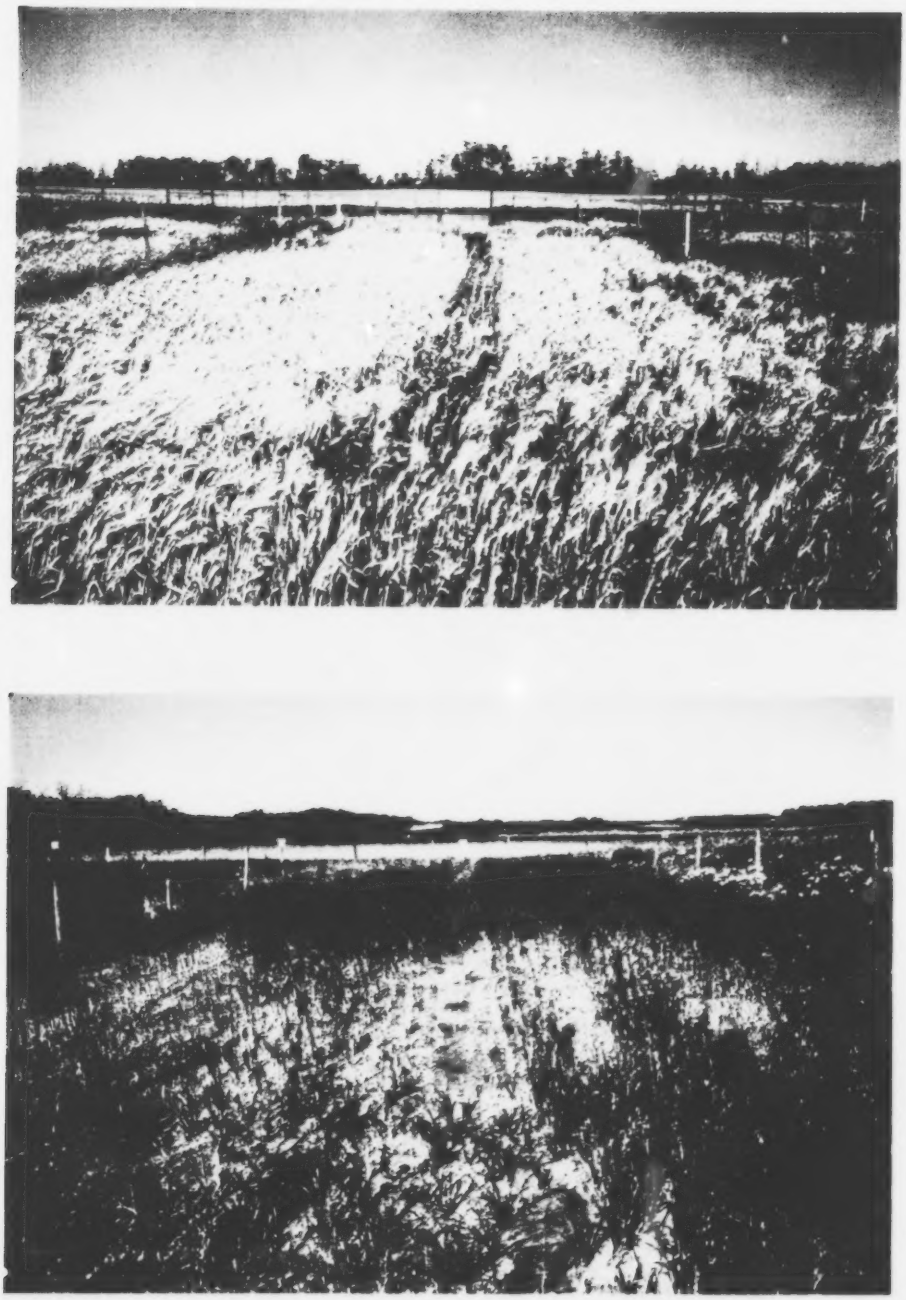

Figure 21. Growth of barley in 1988, 3 years after the last application of oily waste to Lloydminster land treatment plot 5W (top, sludge loading factor 2) and plot 6E (bottom, sludge loading factor 3).

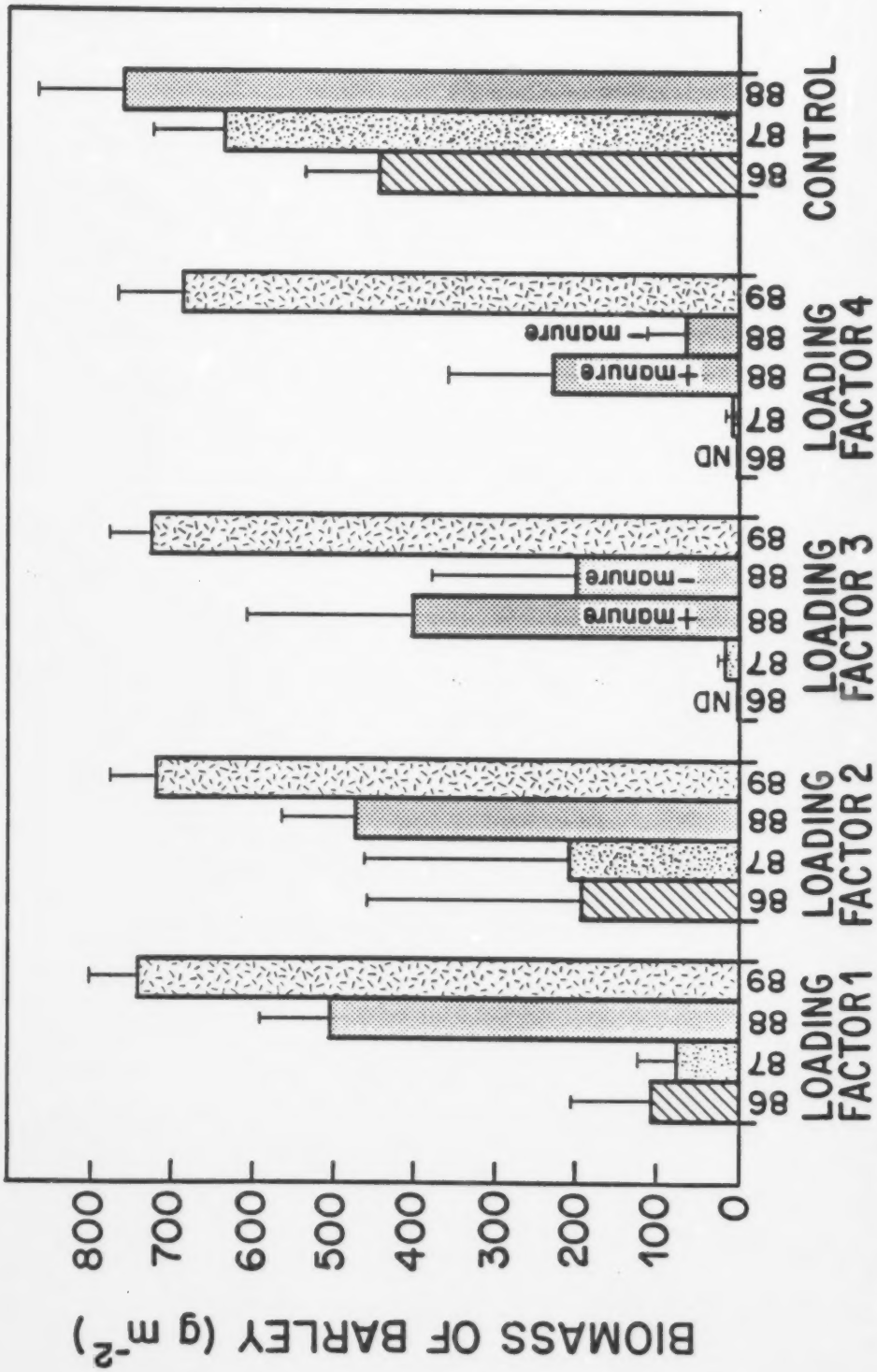


Figure 22. Yield of barley planted on the Lloydminster land treatment plots and on oil-free soil one to four years after the last application of oily wastes. Loading factors are the relative amounts of oil applied (1 = low, 4 = high). Manure applied to half the plots in 1988. Error bars are S.D., n = 4. ND = not determined due to very low biomass.

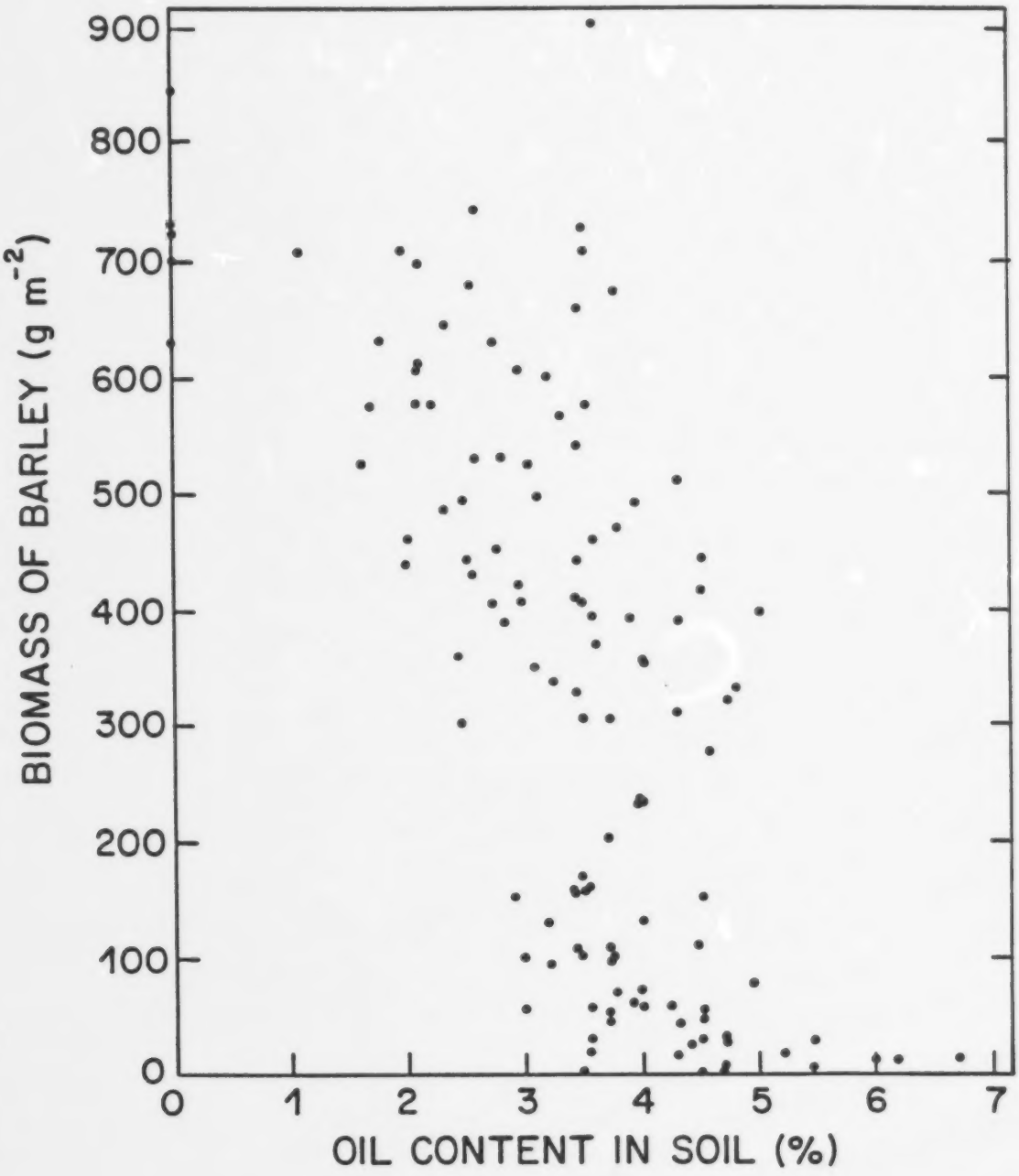


Figure 23. Relationship between soil oil content and barley biomass of clip plots on Lloydminster land treatment plots 3 years after the last application of oily wastes (1988).

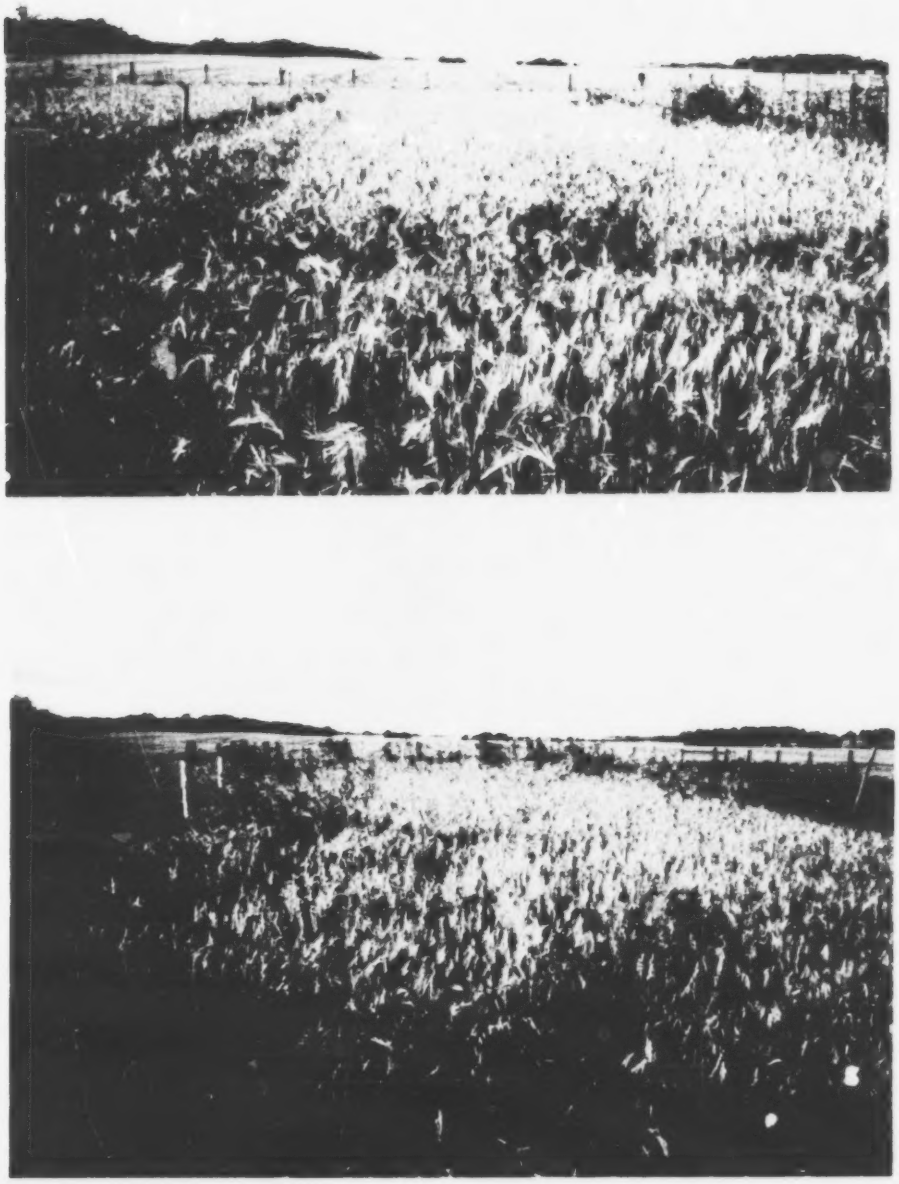

Figure 24. Growth of barley in 1989 4 years after the last application of oily wastes to Lloydminster land treatment plot 6E (top, sludge loading factor 3) and plot 8E (bottom, sludge loading factor 4).

### 8.2.2 Soil Inorganic Chemistry and Plant Growth

The soil SAR, electrical conductivity, chloride and other cation and anion values remained above those of the untreated soil throughout the study (Table 29). In general, values gradually decreased with time and in 1989 salt concentrations were relatively low. The addition of manure had no obvious effect on any of the chemical parameters measured, including oil content.

In 1988, when barley growth was often poor, soil chemistry was studied in the seed germination zone. The values for electrical conductivity and chloride concentrations were much higher in the surface 2 cm of soil than in the bulk samples in plots where growth was strongly inhibited, but similar and low in the plot exhibiting good growth (Table 30).

Potentially toxic metals were measured in four oily sludge treated plots exhibiting poor to good growth and in the untreated soil (Table 31). In general, metals concentrations were higher in the treated soils but differences were small.

### 8.2.3 Heavy Metals in Barley

Concentrations of all metals in both grain and straw were not elevated in plants grown in sludge-treated soil as compared to the control plants with the exception of Fe (Table 32). Fe was exceptionally high in plants from one plot; however these plants were stunted and would not normally be harvested.

### 8.2.4 Recovery of Spiked Standards from Barley

The spiking of the barley was an essential measure to determine if the procedures used in the risk assessments were capable of detecting organic contaminants in plant tissues. The seven deuterated standards were all detected in the appropriate fractions. Naphthalene, anthracene, dibenzothiophene, and chrysene were recovered in the aromatic fraction, hexadecane (and sometimes naphthalene) in the aliphatic fraction, phenol in the acidic fraction, and quinoline in the basic fraction. Naphthalene probably eluted with the aliphatics when hexane was run through the alumina column, so in subsequent fractionations (those reported in Section 8.2.5) hexane was avoided.

Table 29. Comparison of soil (0 - 15 cm) chemistry of West plots (sludge added 3X), East plots (sludge added 4X), East plots with and without manure added in 1988, and untreated (control) field.

| Chemical parameter | West plots | | | East plots (- manure 1988) | | | East plots (+ manure 1988) | Control | |
|---|---|---|---|---|---|---|---|---|---|
| | 1987 | 1988 | 1989 | 1987 | 1988 | 1989 | 1988 | 1987 | 1988 |
| pH | 7.4 | 7.3 | 7.5 | 7.3 | 7.2 | 7.4 | 7.2 | 7.6 | 6.0 |
| SAR | 4.3 | 2.4 | 3.3 | 4.4 | 3.0 | 2.7 | 2.5 | 0.3 | 1.9 |
| Ec, dS $m^{-1}$ | 3.0 | 1.6 | 2.2 | 2.7 | 1.7 | 2.3 | 1.7 | 0.8 | 0.4 |
| Cl, m.e. $L^{-1}$ | 14.9 | 4.1 | 6.4 | 11.0 | 5.0 | 4.9 | 4.1 | 0.2 | 0.1 |
| $NO_3$, m.e. $L^{-1}$ | 0.3 | 0.6 | <0.1 | 0.1 | 0.3 | 0.9 | 0.1 | 0.3 | 1.2 |
| Na, m.e. $L^{-1}$ | 14.3 | 5.9 | 7.9 | 13.5 | 7.1 | 8.0 | 6.1 | 0.6 | 0.3 |
| $SO_4$, m.e. $L^{-1}$ | 10.1 | 4.3 | 5.2 | 9.9 | 5.0 | 5.9 | 5.0 | 0.7 | 0.5 |
| Ca, m.e. $L^{-1}$ | 14.7 | 8.0 | 7.7 | 13.1 | 8.5 | 8.8 | 8.7 | 6.5 | 1.9 |
| Carbon, % | 5.8 | 6.0 | 6.6 | 6.5 | 5.4 | 6.8 | 6.1 | 2.1 | 2.7 |
| Oil content, % | 3.8 | 2.9 | 2.8 | 5.4 | 3.8 | 3.5 | 4.0 | 0 | 0 |

Table 30. Soil pH, total carbon, electrical conductivity, chlorides and sodium adsorption ratio in 1987 of the 0-2 and 0-10 cm depths from three plots treated with oily sludge. Data are means ± SD, n = 4.

| Plot | Soil depth (cm) | Barley Yield ($g\ m^{-2}$) | pH | Ec ($dS\ m^{-1}$) | SAR | Total Carbon % | Cl ($m.e.\ L^{-1}$) |
|---|---|---|---|---|---|---|---|
| 5W | 0-2 | 29 | 7.1 ± 0.1 | 7.0 ± 2.7 | 5.5 ± 2.0 | 6.7 ± 0.8 | 40 ± 24 |
| 5W | 0-10 | - | 7.1 ± 0.1 | 3.4 ± 0.8 | 4.5 ± 0.9 | 6.1 ± 0.8 | 17 ± 7 |
| 7W | 0-2 | 61 | 7.1 ± 0.1 | 3.7 ± 1.2 | 2.7 ± 0.9 | 7.0 ± 0.2 | 12 ± 7 |
| 7W | 0-10 | - | 7.5 ± 0.3 | 1.9 ± 0.3 | 2.7 ± 0.5 | 6.3 ± 0.7 | 5 ± 1 |
| 8W | 0-2 | 403 | 7.2 ± 0.1 | 2.1 ± 0.6 | 1.5 ± 0.5 | 5.9 ± 0.5 | 6 ± 4 |
| 8W | 0-10 | - | 7.7 ± 0.1 | 1.4 ± 0.3 | 2.0 ± 0.6 | 5.5 ± 0.4 | 4 ± 2 |

With acetonitrile extractant, phenol was not the only standard in the acidic fraction. Small amounts (7% on average) of the other standards, except quinoline, were also present. The first extraction procedure in the fractionation process attempted to separate neutral and basic species from acidic species. This was accomplished by shaking the plant extract, in acetonitrile, with methylene chloride and aqueous base. The presence of the acetonitrile may have resulted in inefficient partitioning of the standards into the organic phase. Acetonitrile is highly soluble in both water and methylene chloride, enhancing the affinity of the neutral standards for the aqueous phase. Once in the aqueous phase with the supposedly acidic components, they will be recovered in a subsequent extraction. This slight transfer of

Table 31. DTPA extractable metals from Lloydminster soils (0 - 15 cm) treated with oily sludges which supported poor to good growth of barley in 1987. Data are means ± SD, n = 5.

| Plot | Barley yield ($g\ m^{-2}$) | Fe | Cu | Zn | Pb | Mn | Cd | Ni |
|---|---|---|---|---|---|---|---|---|
| | | $mg\ kg^{-1}$ | | | | | | |
| 4W | 126 ± 129 | 34 ± 5 | 0.51 ± 0.04 | 1.7 ± 0.1 | 1.7 ± 0.5 | 6.4 ± 0.5 | 0.07 ± .01 | 0.8 ± .02 |
| 6W | 35 ± 14 | 38 ± 10 | 0.60 ± 0.02 | 1.9 ± 0.1 | 1.5 ± 0.2 | 8.3 ± 1.2 | 0.06 ± .01 | 0.9 ± .04 |
| 7W | 69 ± 48 | 42 ± 4 | 0.55 ± 0.02 | 1.7 ± 0.2 | 1.4 ± 0.1 | 8.3 ± 2.1 | 0.05 ± .01 | 0.9 ± .03 |
| 8W | 403 ± 272 | 32 ± 1 | 0.58 ± 0.10 | 2.0 ± 0.1 | 1.4 ± 0.3 | 5.2 ± 0.5 | 0.08 ± .01 | 0.9 ± .02 |
| Control | 634 ± 87 | 26 ± 2 | 0.31 ± 0.01 | 0.6 ± 0.1 | 0.5 ± 0.1 | 3.2 ± 0.1 | 0.04 ± 0 | 0.7 ± .04 |

Table 32. Heavy metal contents of barley straw and grain grown in oil-free and oily sludge treated soil at Lloydminster in 1987. Data are means ± SD, n = 5.

| Plot | | Barley Yield ($g\ m^{-2}$) | Fe | Cu | Zn | Pb | Mn | Cd | Ni |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $mg\ kg^{-1}$ | | | | |
| Control | grain | 380 ± 54 | 45 ± 18 | 6 ± 3 | 23 ± 4 | 7 ± 2 | 17 ± 1 | <1 | 11 ± 12 |
| Control | straw | 251 ± 30 | 58 ± 11 | 3 ± 1 | 8 ± 2 | 3 ± 1 | 15 ± 2 | <1 | 3 ± 1 |
| 6W | grain | 15 ± 9 | 150 ± 100 | 4 ± 2 | 18 ± 2 | 6 ± 2 | 40 ± 7 | <1 | 5 ± 4 |
| 6W | straw | 20 ± 8 | 910 ± 192 | 3 ± 2 | 11 ± 1 | 3 ± 1 | 81 ± 11 | <1 | 5 ± 1 |
| 8W | grain | 159 ± 101 | 14 ± 19 | 4 ± 2 | 30 ± 11 | 10 ± 3 | 26 ± 2 | <1 | 7 ± 4 |
| 8W | straw | 236 ± 169 | 197 ± 131 | 2 ± 1 | 13 ± 3 | <2 | 46 ± 6 | <1 | 1 |

neutral substances into aqueous solution was at least partially rectified by reducing the volume of the original acetonitrile extract before proceeding with the fractionation steps. This change was incorporated in all subsequent analyses.

The recovery of the more volatile standards was relatively low and variable (Table 33). The recoveries of naphthalene covered a broad range, possibly due to the long lapse of time between the completion of the separation procedure and the GC analysis. Anomalous behaviour was seen in the recovery of chrysene which showed a return in excess of 100%. This may have been caused by the existence of some component, either extracted from the barley or present as an impurity, which co-eluted with chrysene. The blank aromatic run exhibited a peak with the same retention time as that of chrysene.

Overall, the recoveries from the Polytron-acetonitrile extraction technique were generally good and superior to those from the methylene chloride-Soxhlet extraction technique. Methylene chloride did not appear to be an efficient solvent for the extraction of wide variety of chemical compounds from plant material. Acetonitrile accomplished the task not only more effectively but also more quickly.

Table 33. Recoveries of deuterated standards following extractions with acetonitrile and sonification or methylene chloride and Soxhlet extraction. Data are means ± SD, n=3 or 1.

| Standard | Acetonitrile % Recovery | Methylene Chloride % Recovery |
|---|---|---|
| naphthalene $d_8$ | 55.3 ± 30.0 | 72.1 |
| dibenzothiophene $d_8$ | 90.0 ± 7.4 | 32.1 |
| anthracene $d_{10}$ | 83.6 ± 10.4 | 29.8 |
| chrysene $d_{12}$ | 125.1 ± 9.9 | 11.0 |
| hexadecane $d_{34}$ | 98.7 ± 0.7 | 57.7 |
| phenol $d_6$ | 81.0 ± 9.4 | 2.9 |
| quinoline $d_7$ | 97.9 ± 0.5 | 68.4 |

### 8.2.5 Plant Uptake of Organic Contaminants

The plant extracts were separated into acidic, basic, aliphatic, aromatic and polar fractions to determine if undesirable organic compounds had accumulated in plant tissues grown on soil treated with oily sludges. Although a large number of compounds could be identified in the extracts, there was no indication that the plants had taken up potentially harmful chemicals (Tables 34 and 35). A larger number of compounds were present in the immature fresh-frozen samples than in the mature air-dry samples. Nearly all the substances identified contained hydroxyl, aldehydic and/or carboxylic acid functional groups. Known catabolic pathways for the degradation of aromatic hydrocarbons generally involve an initial hydroxylation step, followed either by progressive oxidations, or by ring cleavage and oxidation at the cleavage site, depending on the original structure. Most of the aromatic acids and phenolic and benzaldehydic derivatives listed in the tables are expected biodegradation products. Although not all the compounds extracted from plants grown on oily soil were also present in the control plants, almost all are recognized as naturally occurring substances, or at least as closely related to or derived from naturally occurring substances. It is not likely that plant uptake from the soil is responsible for their presence.

### 8.2.6 Chemical Degradation of Asphaltenes

Fractionation of the toluene extracted oil from Lloydminster Plot 6E resulted in 18.2% asphaltenes, 28.6% oil, 27.1% resin-1, and 20.7% resin-2. The asphaltene fraction was partially depolymerized with phenol and the toluene-soluble products fractionated into neutral, phenolic/acid, polar and basic fractions which were analysed by GC/MS. The neutral fraction was further chromatographed to produce a neutral aromatic and a neutral polar fraction prior to GC/MS analysis.

The neutral aromatic fraction revealed the greatest variety of aromatics, generally falling into the categories of naphathlenes, benzofurans, benzothiophenes and xanthenes. The acidic/phenolic and polar fractions were known to be almost identical from their GC traces, but to verify this, their mass spectra were compared. Both contained a series of alkyl-substituted phenols and a series of alkyl-connected

Table 34. GC/MS analysis of extracts of air-dried mature barley grain and straw in sludge treated plot 4E (oil 4.1%, plant growth 35% of control) and in the untreated field in 1988.

| Compounds identified | Control grain | Control straw | Plot 4E grain | Plot 4E straw |
|---|---|---|---|---|
| | | | $\mu g\ g^{-1}$ | |
| Aliphatic acids | | | | |
| $C_4H_9$-COOH | 0.5 | - | - | 0.4 |
| $C_5H_{11}$-COOH | 14.2 | - | 14.0 | 5.3 |
| $C_6H_{13}$-COOH | 0.3 | - | - | 0.3 |
| $C_7H_{15}$-COOH | 0.7 | 1.1 | 2.1 | 3.0 |
| $C_8H_{17}$-COOH | - | - | - | 1.4 |
| $C_9H_{19}$-COOH | 6.1 | - | - | 2.6 |
| $C_{10}H_{21}$-COOH | 23.4 | 8.1 | 45.0 | 6.1 |
| $C_{11}H_{23}$-COOH | - | - | 3.2 | 7.4 |
| $C_{12}H_{25}$-COOH | 0.8 | - | - | 0.6 |
| $C_{13}H_{27}$-COOH | 2.2 | 12.2 | 8.8 | 20.9 |
| $C_{14}H_{29}$-COOH | - | 1.4 | - | 0.5 |
| $C_{15}H_{31}$-COOH (palmitic acid) | 88.2 | 66.6 | 137.3 | 9.5 |
| $C_{17}H_{31}$-COOH (linoleic acid) | 2.7 | 91.8 | 14.0 | 8.7 |
| $C_{17}H_{35}$-COOH (stearic acid) | 0.9 | 2.3 | 0.6 | - |
| $C_{17}H_{31}$-CHO | - | 91.8 | - | - |
| Phenolic and Benzaldehydic Derivatives | | | | |
| hydroxybenzaldehyde | - | - | - | 0.8 |
| vanillin | - | - | - | 1.1 |
| Miscellaneous Compounds | | | | |
| acetonaphthone | - | - | - | 0.2 |
| $C_{14}$, $C_{15}$, $C_{16}$, and $C_{17}$ paraffins | 1.4 | 0.8 | 0.1 | 2.0 |
| a heptadecadien-2-one | - | - | - | 9.8 |

Table 35. GC/MS analysis of extracts of fresh-frozen immature barley grain and straw in sludge treated plot 5W (soil oil 3.1%, plant growth 53% of control), sludge treated plot 8W (soil oil 2.7%, plant growth 82% of control) and in the untreated field in 1988.

| Compounds identified | Control grain | Control straw | 8W grain | 8W straw | 5W grain | 5W straw |
|---|---|---|---|---|---|---|
| | | | $\mu g\ g^{-1}$ | | | |
| Aliphatic acids | | | | | | |
| $C_4H_9$-COOH | 0.5 | - | - | - | 0.1 | - |
| $C_5H_{11}$-COOH | 4.5 | - | - | - | 2.5 | - |
| $C_6H_{13}$-COOH | 0.1 | - | 0.1 | - | 0.9 | - |
| $C_7H_{15}$-COOH | 0.4 | 0.5 | 0.3 | - | 0.9 | 0.7 |
| $C_8H_{17}$-COOH | - | - | - | 0.2 | 0.3 | - |
| $C_9H_{19}$-COOH | - | - | - | 0.5 | 0.1 | - |
| $C_{10}H_{21}$-COOH | 1.8 | 0.4 | 0.7 | 2.4 | 3.8 | 1.7 |
| $C_{11}H_{23}$-COOH | 0.3 | 2.0 | - | 2.7 | 0.7 | 2.3 |
| $C_{13}H_{27}$-COOH | 1.1 | 0.4 | - | 1.0 | 1.5 | 1.7 |
| $C_{14}H_{29}$-COOH | - | - | - | - | 0.3 | - |
| $C_{15}H_{31}$-COOH (palmitic acid) | 8.6 | 7.5 | 1.5 | 4.0 | 15.0 | 4.4 |
| $C_{17}H_{31}$-COOH (linoleic acid) | 20.5 | 1.2 | - | 1.6 | 22.0 | 0.3 |
| $C_{17}H_{35}$-COOH (stearic acid) | 0.1 | - | - | - | - | - |
| Aromatic Acids | | | | | | |
| benzoic acid | 0.4 | 0.6 | 0.2 | 5.1 | 1.1 | 2.0 |
| phenyl acetic acid | 0.2 | - | 1.6 | 2.3 | 5.5 | - |
| cinnamic acid | 0.4 | - | - | - | 1.0 | - |
| vanillic acid | - | - | - | - | 0.3 | - |

continued...

Table 35. (Continued).

| Compounds identified | Control grain | Control straw | 8W grain | 8W straw | 5W grain | 5W straw |
|---|---|---|---|---|---|---|
| | | | µg $g^{-1}$ | | | |
| Phenolic and Benzaldehydic Derivatives | | | | | | |
| methoxy phenol | - | - | - | 0.3 | 0.1 | 0.3 |
| phenyl acetaldehyde | - | 1.4 | - | 1.5 | 1.0 | 4.7 |
| hydroxy methylacetophenone | 0.1 | - | 0.7 | 5.2 | 5.3 | 11.6 |
| hydroxy benzaldehyde | - | 0.6 | - | 0.7 | 0.2 | 1.3 |
| vanillin | 0.4 | 3.6 | 0.1 | 4.2 | 0.8 | 5.5 |
| 1-(hydroxy phenyl)-2-propen-1-one | - | - | - | - | - | 0.7 |
| 3-(3,5-dimethoxy-4-hydroxyphenyl) propionaldehyde | - | 1.8 | - | 1.8 | - | 6.3 |
| 1-(hydroxy methoxyphenyl)-2-propen-1-one | - | - | - | - | - | 1.1 |
| butyl phenol | - | 0.3 | - | - | 0.2 | 1.5 |
| syingaldehyde | - | 0.7 | - | 1.1 | 0.2 | 2.6 |
| coniferyl alcohol | - | - | - | 7.3 | 4.3 | 24.2 |
| 1-(hydroxy methoxyphenyl)-3-hydroxy-1-propanone | - | - | - | - | - | 0.4 |
| 1-(dimethoxyhydroxylphenyl)-2 propen-1-one | - | - | - | - | - | 0.4 |
| sinapaldehyde | - | - | - | - | - | 1.1 |

continued...

Table 35. (Concluded).

| Compounds identified | Control grain | Control straw | 8W grain | 8W straw | 5W grain | 5W straw |
|---|---|---|---|---|---|---|
| | | | μg $g^{-1}$ | | | |
| Miscellaneous Compounds | | | | | | |
| $C_{15}$,$C_{16}$,$C_{17}$ and $C_{18}$ paraffins | 1.0 | 1.0 | - | 0.3 | - | 1.7 |
| $C_{20}H_{38}$ (eicosynes?) | - | - | - | - | 139.0 | 174.3 |
| indol | 0.1 | - | - | 0.3 | - | 0.2 |
| 4-methoxythioanisole | - | - | - | - | 0.6 | 0.9 |
| (4-tolyl) butyl sulfide | - | 8.2 | - | - | - | 2.0 |
| 2-6-dimethoxyl-1,4-benzoquinone | - | - | - | - | - | 0.7 |
| dimethoxy acetophenone | - | - | - | - | - | 0.3 |
| butyl phenyl ether | - | - | - | - | 0.1 | 0.8 |
| acetonaphthone | - | 0.2 | - | 0.5 | - | 0.3 |
| butyl phenyl ketone | - | 0.2 | - | - | - | - |

diphenolic species. Longer series were detected in the polar fraction, accounting for the only, but minor, difference between the two. The neutral polar fraction was comprised predominantly of carbazoles, and the basic fraction of unimportant by-products of the reaction (there were no basic substances in evidence).

The asphaltene degradation products contained the following chemicals.

1. Aliphatic side chains originally attached to aromatic units. These varied from $CH_3$ to $C_7H_{15}$ in length, and were either linear or non-linear. Some cycloalkyl sidechains were also detected, e.g., cyclopentyl and cyclohexyl. These aliphatic appendages to aromatic units accounted for 1% of the mass of the asphaltenes.
2. Aliphatic bridges originally connecting two aromatic units. These bridges consisted of one to five carbon atoms and were either linear or branched. These connections accounted for 0.3% of the asphaltenes.
3. Aliphatic bridges originally connecting three aromatic units. These were one carbon connections where one of the aromatic units was sometimes phenyl. These fragments of the asphaltene structure accounted for 0.008%.
4. Aromatic units originally attached to the asphaltene matrix via some form of aliphatic bridge or possibly present as separate entities bearing aliphatic sidechains. In some instances, aromatic structures were identified having one or more methyl groups; this is not unusual since phenol does not readily remove methyl substituents.

The types of aromatic compounds which were easily degraded from the asphaltene structure included carbazoles (84 mg $L^{-1}$), benzofurans (38 mg $L^{-1}$), naphthalenes (122 mg $L^{-1}$), benzothiophenes (364 mg $L^{-1}$), naphthols (248 mg $L^{-1}$), flav-3-enes (56 mg $L^{-1}$), disulphides (22 mg $L^{-1}$), and thianthrenes (46 mg $L^{-1}$).

8.2.7 Results: Groundwater and Surface Water Quality

8.2.7.1 Geology. A total of 22 boreholes at eleven sites were drilled to define the shallow geology beneath the plots (Figure 25). At one location, P493, a continuous core was collected to facilitate detailed description of geology and structure.

The site was underlain by fine textured till to a depth of at least 9 m (greatest drilling depth reached). The till, grey, grading to grey-brown with depth was dense, plastic and contained numerous pebbles and fine-grained sand lenses. Visual examination of the core from P493 suggested the presence of fractures to a depth of at least 2.5 m. The fractures were commonly coated with calcite and/or iron staining.

8.2.7.2 Groundwater flow. Water levels were recorded on twelve occasions. Water level data suggests that the predominant direction of shallow groundwater flow was toward the east under the influence of a shallow hydraulic gradient. Water levels from the piezometer nest located in the northeast corner of the site indicated that the site was located in a groundwater recharge area. That is, the predominant direction of groundwater flow is downward. A vertical hydraulic gradient of 0.6 was estimated from available data.

Water levels in the water table wells reached a static equilibrium slowly after well installation. A noticeable increase in water levels was evident in July to September recordings. These increases are attributable to high precipitation in the June to August period. Water levels tend to decrease in fall and winter due to lack of recharge. The average annual water table fluctuation was 1.5 m.

Hydraulic conductivity tests were conducted on piezometers P178, P500 and P501. In general the hydraulic conductivity (K) of surficial materials at the site was low. K values ranged from $10^{-5}$ to less than $10^{-6}$ cm $sec^{-1}$. Considerable variations in the K values obtained within the site reflect the presence of the many small sand and silt deposits throughout the clay till overburden.

Groundwater velocity was calculated to vary between 1 - 100 cm per year horizontally and 50 - 100 cm per year vertically.

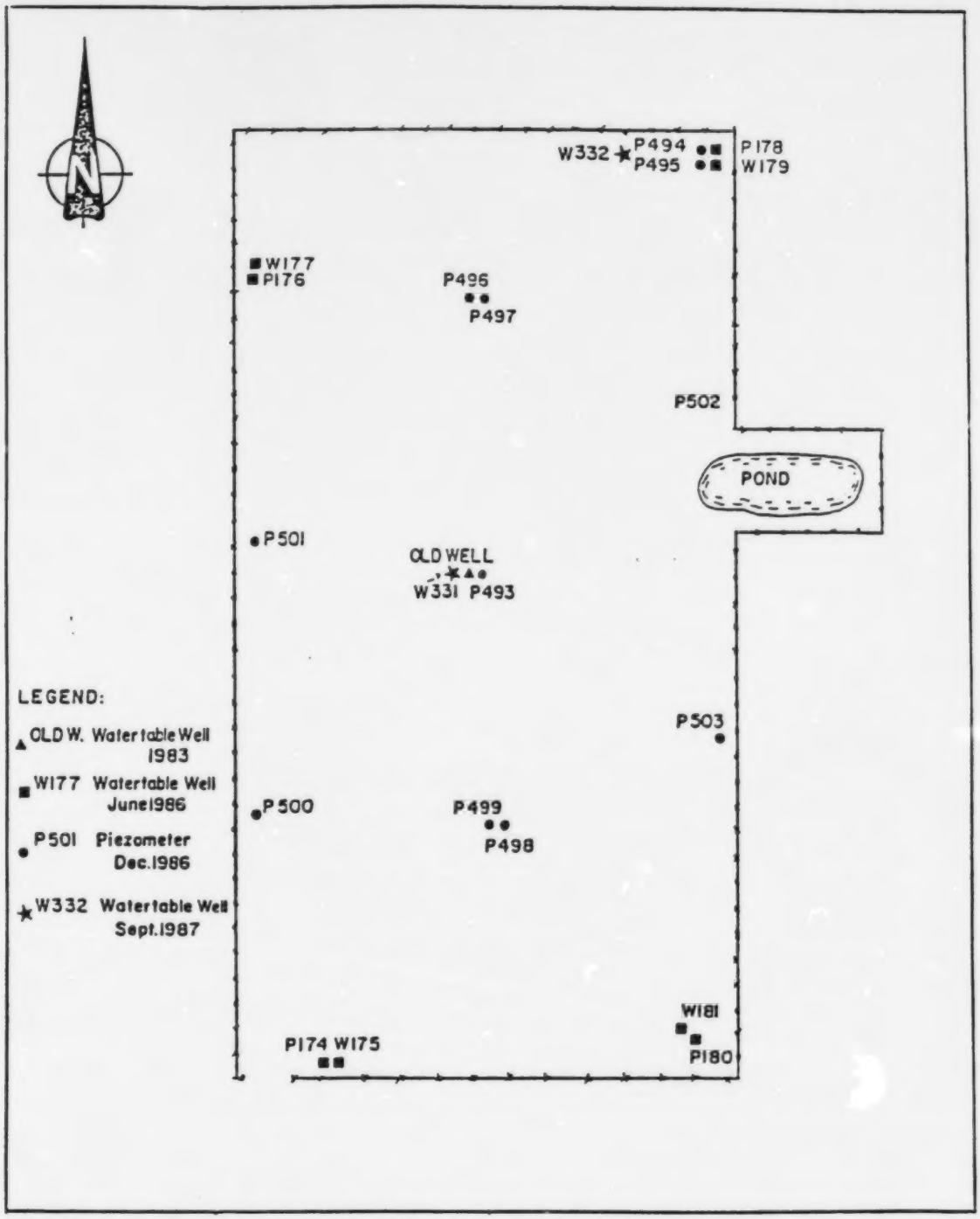


Figure 25. Lloydminster land treatment study site plan.

8.2.7.3 Groundwater chemistry. Groundwater samples were collected for chemical analysis on September 11, and December 3, 1986, on January 6, April 14, September 2, and December 1, 1987, on July 15, 1988 and on August 8, 1989. See Appendix for individual well data.

Analytical data indicate that shallow groundwater chemistry was highly variable, reflecting the complex mineralogy of the till. To a depth of approximately 6 m, groundwater varied from the calcium/magnesium - bicarbonate to the calcium/magnesium - sulphate type. The total dissolved solids concentration (TDS) varied from 480 - 7000 mg $L^{-1}$, with a mean of 3000 mg $L^{-1}$ Groundwater from the piezometers completed at the 9 m depth is the calcium/magnesium - sulphate type with a TDS concentration varying from 2500 - 4100 mg $L^{-1}$.

Total carbon (TOC) concentrations in groundwater varied from 10 to 75 mg $L^{-1}$, with a mean of 25 mg $L^{-1}$. This indicates that groundwater had a relatively low organic load.

Detailed information about shallow groundwater chemistry prior to establishment of the plots is not available. However samples collected from a well installed prior to sludge-nutrient application were analyzed for key indicators of contamination (see Table 25). A comparison of 1986-89 analytical data with pre-sludge application groundwater chemistry data indicates that the chloride and nitrate levels increased substantially, suggesting groundwater contamination. The probable source of the chloride was the aqueous portion of the sludge, and the source of the nitrate was probably the fertilizer applied to the site.

The chloride ion was used to obtain information about the areal extent of groundwater contamination. Chloride is a suitable indicator because it has a low ambient concentration at the site (<10 mg $L^{-1}$), is relatively inert and extremely mobile in the aqueous environment. Figure 26 indicates that shallow groundwater was contaminated beneath and down gradient from the plots. Groundwater tended to be more contaminated in the northeastern half of the plots, probably since this area received four applications of sludge. The large amount of sludge applied to the east half of plot 8 (in the northeast corner of the demonstration plots) may account for unusually high chloride levels in groundwater from P497, P495 and W179.

Due to the strong attenuation capacity of the surficial materials, groundwater contamination decreased rapidly with depth (Figure 27).

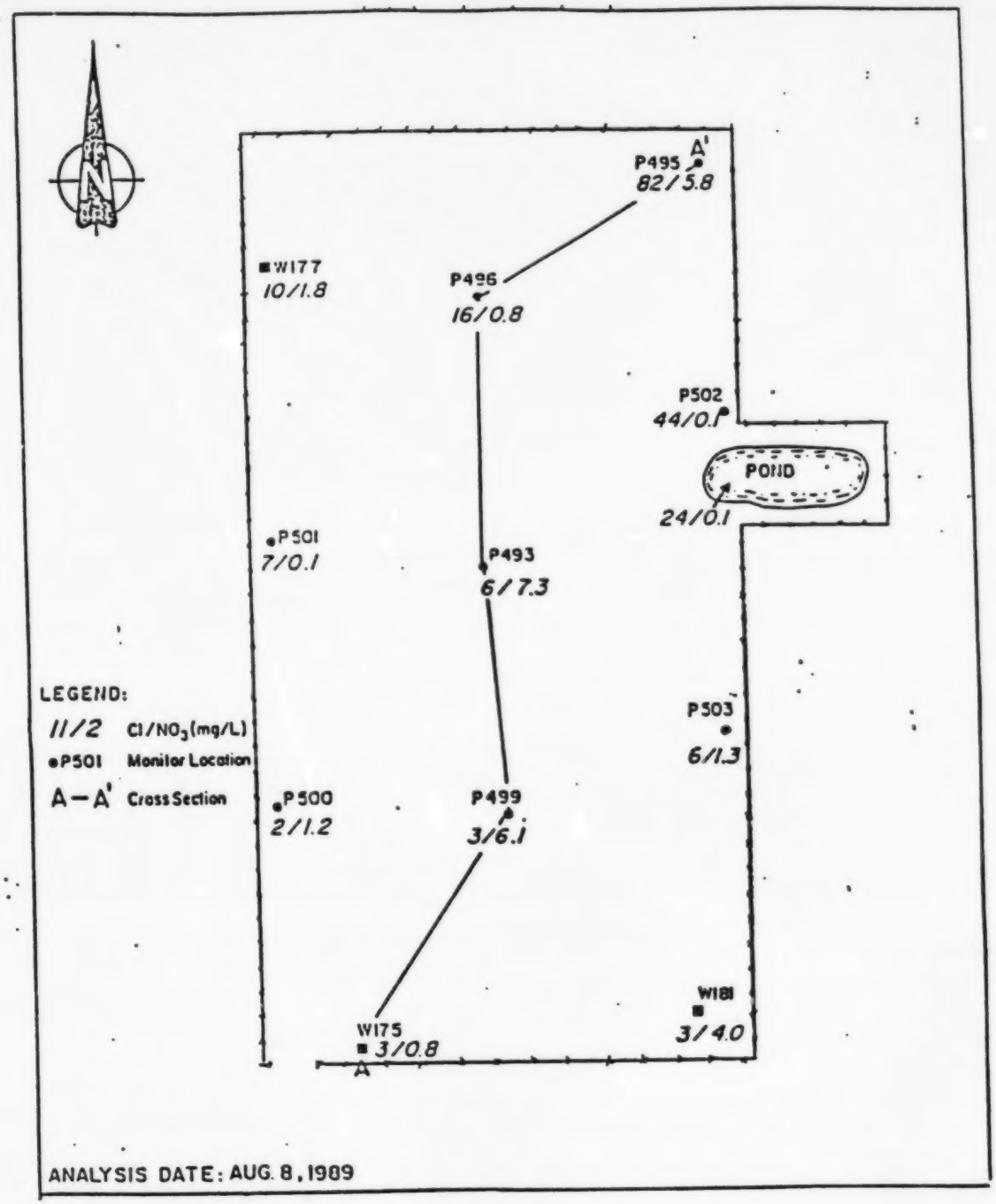


Figure 26. Areal distribution of chloride and nitrate concentrations in shallow groundwater - August 8, 1989.

This was reflected in the August, 1989 analysis of water from water table - piezometer nests P178, P496 - P497, and W179 which show decreasing concentrations of chlorides with depth. An exception appears to be W OLD, which is the deepest well at the site. Completion data for this well are not available, but the well is thought to be slotted throughout the length of the casing and not properly sealed at the surface. Thus the high concentration of chloride and organics might be due to surface water entering the well.

Chemical analysis data from August, 1989 show generally similar values to that of July, 1988. However, concentrations of ammonium and nitrate nigrogen as well as iron, manganese, lead and C.O.D. were somewhat lower in 1989. Magnesium and sulphate values were slightly elevated. Samples from wells W331 and the adjacent W-old show significantly higher chloride concentration for 1989.

Hydrocarbon scans on groundwater samples collected on February 1990 from well WW331 and W332 (stainless steel-teflon wells with dedicated sampling hoses) showed no traces of hydrocarbons (detection limit was 0.05 mg $L^{-1}$).

In general, shallow groundwater was of poor quality with several parameters exceeding upper limits established in Canadian Drinking water standards (C.D.W.S.) (Health and Welfare Canada, 1976). It is interesting to note that the lead concentration in groundwater exceeded the C.D.W.S. in almost every analysis. It is likely that this was is a natural occurrence although it may have been attributable to contamination.

8.2.7.4 Surface water chemistry. Analysis of a sample collected from the runoff pond, prior to sludge application in 1982 indicated that the water had a very low organic and inorganic load (Peake et al. 1985). Immediately after application of the sludge and nutrients, the concentrations of chloride, nitrate and sulphate increased dramatically (Figure 28). The analyses of pond water samples collected on November 4, 1986, September 2, 1987, July 15, 1988 and August, 1989 indicate that the concentrations of chloride, nitrate and sulphate have steadily decreased since the last sludge-nutrient application in 1985, but are still above background levels.

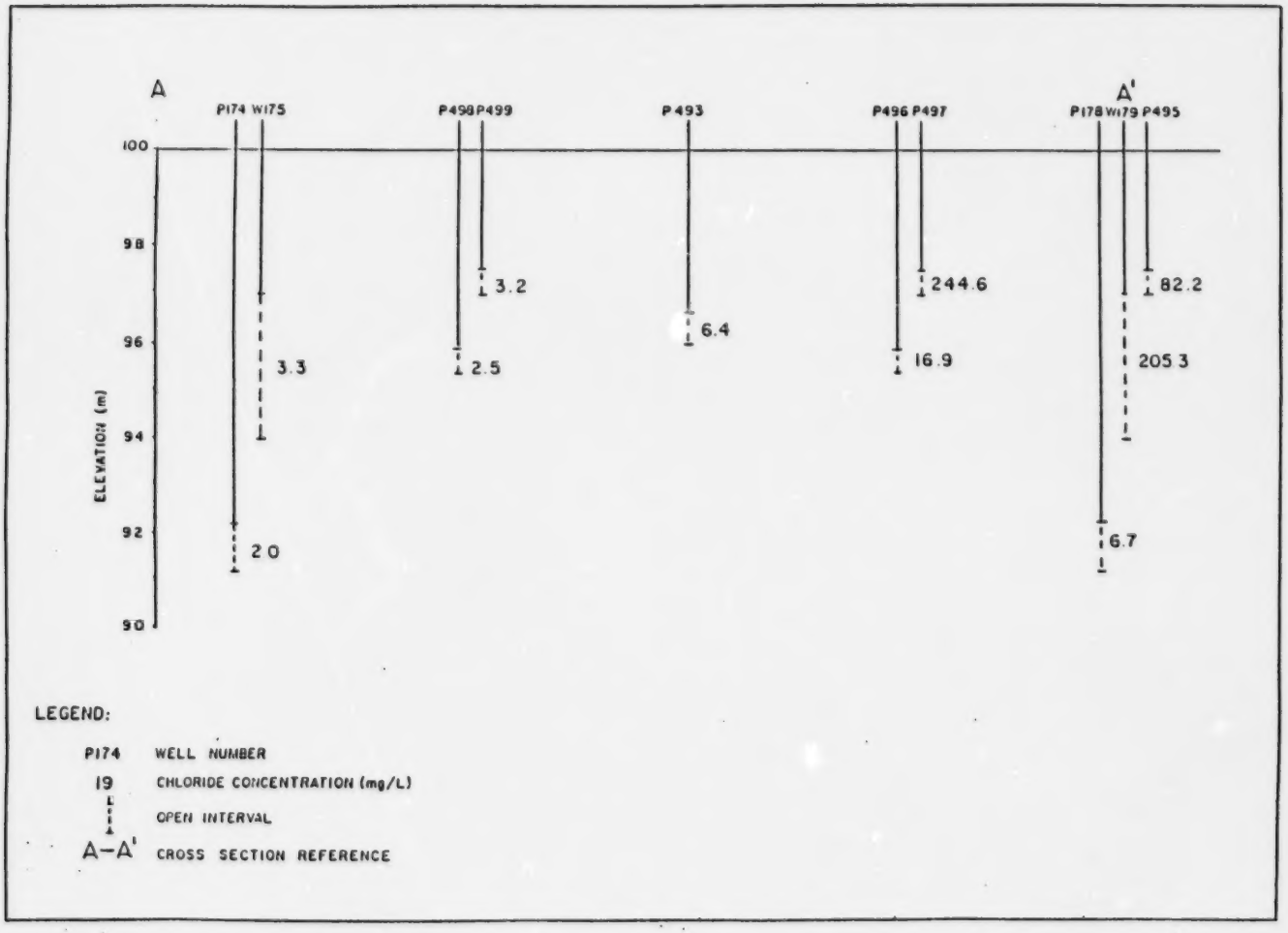


Figure 27. Chloride concentration vs. depth, August 8, 1989.

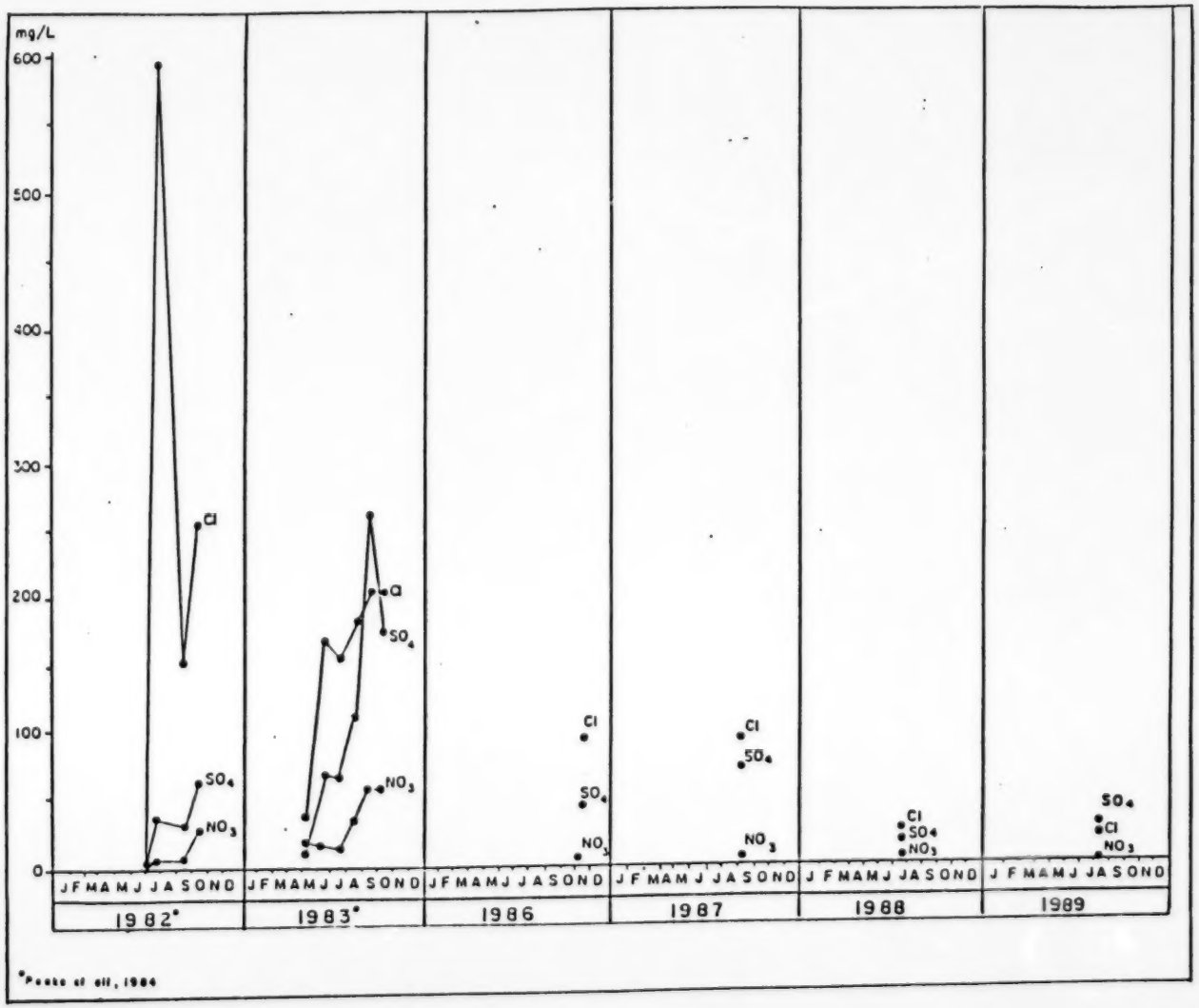


Figure 28. Cl, $NO_3$, and $SO_4$ concentration variations in pond water.

# 9. CONCLUSIONS

## 9.1 OIL DEGRADATION

It was demonstrated that large quantities of non-utilizable oily wastes could be disposed of using the land treatment technique at four geographic sites in Alberta. It was assumed that the major factor responsible for the disappearance of the hydrocarbons was microbial decomposition although it is recognized that volatilization of low molecular weight fractions may have constituted a significant role, especially immediately following applications of oily sludges. The amount degraded was dependent upon the quantity added and the composition of the oily sludges, and the soils appeared to have high loading capacities (Table 36). It would appear that levels up to or above 10% in the soil (220,000 kg $ha^{-1}$) will permit rapid degradation. The largest quantity degraded (plus volatilization) in one year was 136,000 kg $ha^{-1}$ at Drayton Valley and even with the heavy Lloydminster oil, a maximum of 59,000 kg $ha^{-1}$ was degraded. Degradation continued at moderately rapid rates for at least several years after oil additions had ceased. The recommended loading rates of 10-12% found in this study are significantly higher than the 5% rate recommended by Bartha and Bossert (1984). It is probable that rates much exceeding 10% will inhibit biodegradation (Bartha, 1986) but that rates between 5 and 10% could be maintained by repeated applications to efficiently use land treatment sites.

## 9.2 ASPHALTENE DEGRADATION

It might be expected that the high molecular weight compounds found in oily sludges would accumulate relative to the lighter fractions in the soil due to their low rates of decomposition (Confield and Racz, 1978). It has been observed that the asphaltene fraction may actually increase due to microbial activity and the transformation of other hydrocarbons into asphaltenes (Bossert and Bartha, 1984). However, in this study, the proportion of oil composed of asphaltenes remained relatively constant at about 20% throughout the study. The quantity of asphaltenes in the soil steadily decreased in the final 4

Table 36. Summary of quantities of oil degraded during land treatment at four sites in Alberta. Percentages are oil concentrations at the beginning of the measurement period following applicatons of new oily sludge and oil concentrations at the end of the measurement period.

| Measurement Period | Loading 1 and 2 | | | Loading 3 and 4 | | |
|---|---|---|---|---|---|---|
| | New Oil Added | % Oil | Oil Degraded (kg ha$^{-1}$) | New Oil Added | % Oil | Oil Degraded (kg ha$^{-1}$) |
| | | | GRANDE PRAIRIE | | | |
| 1982-83[1] | + | 2.7→0.8 | 43,000 | + | 2.7→1.0 | 38,000 |
| 1983-84[1] | - | 0.8→0.4 | 9,000 | + | 4.2→1.8 | 53,000 |
| 1984[2] | + | 3.0→1.5 | 31,000 | + | 4.2→2.4 | 52,000 |
| | | | DRAYTON VALLEY | | | |
| 1982-83[1] | + | 11.8→5.9 | 131,000 | + | 11.8→5.6 | 136,000 |
| 1983-84[1] | - | 5.9→4.3 | 34,000 | + | 7.7→5.8 | 43,000 |
| 1984[2] | + | 4.3→2.5 | 39,000 | + | 5.8→4.1 | 37,000 |
| | | | BROOKS | | | |
| 1983-84[1] | + | 5.5→3.9 | 36,000 | + | 5.5→3.6 | 42,000 |
| | | | LLOYDMINSTER | | | |
| 1982-83[1] | + | 1.7→1.4 | 6,000 | + | 1.7→1.5 | 4,000 |
| 1983-84[1] | - | 1.4→1.0 | 10,000 | + | 6.2→3.6 | 59,000 |
| 1984-85[1] | + | 2.6→2.1 | 10,000 | + | 5.3→4.2 | 24,000 |
| 1985[2] | + | 5.2→4.3 | 19,000 | + | 8.3→6.3 | 43,000 |
| 1986-87[3] | - | 4.5→3.8 | 15,000 | - | 6.4→5.4 | 22,000 |
| 1987-88[3] | - | 3.8→2.9 | 20,000 | - | 5.4→3.9 | 33,000 |
| 1988-89[3] | - | 2.9→2.8 | 2,000 | - | 3.9→3.4 | 11,000 |

[1] May to May
[2] May to October
[3] October to October

years at Lloydminster. Although it is anticipated that the decomposition rate of the high molecular weight fraction will decrease and for this fraction to stabilize, it does not appear to be a matter for concern. A simulated chemical degradation study of the asphaltenes resulted in the degradation of a small portion of the structure and was inconclusive for predicting future degradation products and their effects on groundwater comtamination.

## 9.3 FERTILIZATION AND CULTIVATION

Differential fertilization and cultivation treatments were applied to the sites for the first two years of the study and thereafter all plots were treated equally. No effects on any parameters measured could be attributed to the high and low levels of fertilizer or cultivation. However, it is recognized that ample quantities of nitrogen fertilizers must be supplied for efficient and rapid hydrocarbon degradation (Bartha, 1986). In the range of nitrogen used in this study with lower application of oily wastes, Sandvic et al. (1986) clearly demonstrated higher rates of oily sludge degradation when 400 vs. 200 kg N $ha^{-1}$ were used under Norwegian conditions. The positive effects of cultivation on oil degradation rates have never been demonstrated in any field situations but cultivation no doubt benefits soil aeration and breaks up large oil concentrations.

## 9.4 INORGANIC SOIL CHEMISTRY

All the areas were limed prior to oil application to reduce possible leaching of heavy metals and the soil reaction remained above pH 7 for the duration of the study. The addition of sludges generally resulted in elevated levels of chlorides, sodium, and sulphates which gradually declined with time. SAR values at Lloydminster were below those which would be anticipated to cause inhibition of plant growth (Bohn et al., 1979). Electrical conductivities were frequently greater than 2 dS $m^{-1}$ and chlorides were generally between 10 and 20 m.e. $L^{-1}$ at Lloydminster prior to reclamation efforts. Although these values were not excessively high, salts appeared to be a factor in limiting plant growth. Continued reclamation efforts reduced salt concentrations to levels which were noninhibitory to plant growth.

## 9.5 SOIL OIL CONTENT AND PLANT GROWTH

Growth of barley at Lloydminster was strongly inhibited when the soil contained over 5% oil. Below this value, growth was exceedingly variable and some of the variability was due to the synergistic effect of salts. Once salt concentrations were low and mineral nutrition adequate, growth comparable to that on oil-free soil was possible up to 4.5% oil content. It should be noted that the oil was well-weathered, i.e., it had been in the soil for a minimum of 4 years and presumably the most volatile and most biodegradable oil fractions had largely disappeared. Thus the oil present was relatively inactive and with low phytotoxicity potential.

## 9.6 PLANT UPTAKE OF ORGANIC CONTAMINANTS

It did not appear that barley absorbed any oil hydrocarbons from the soil and translocated them to the shoots. Neither immature or mature straw or grain contained any compounds which could not have been of plant origin or other natural products. On the basis of analyses performed in this study, it appears that organic compounds in oil and their degradation products pose no threats for utilization of plants grown in soils treated with oily wastes. Plant uptake of $^{14}C$ labeled naphthalene and anthracene has also been shown to be extremely small under microcosm conditions (Hosler et al., 1990).

## 9.7 HEAVY METALS IN SOILS AND CROPS

Small quantities of Cu, Pb, Zn, Cd, and Ni were introduced with the sludges but they appeared to be in insufficient quantities to cause concern. At Lloydminster 2 years after the last sludge application, levels of extractable metals in oil-treated and untreated soils were nearly identical. Barley grown in these soils contained very similar metal concentrations regardless of oil treatment. Unlike oily sludges from refineries, the oil field wastes used in this study were low in heavy metals and would not contaminate groundwater or enter the food chain. Due to the high soil pH, which remained stable for up to 8 years, the metals exhibited low availability and sludges with higher levels of heavy metals might also be successfully disposed of by land treatment techniques.

## 9.8 MIGRATION OF HYDROCARBONS IN THE SOIL

Oily sludges incorporated into the surface soil remained in place for the duration of the study. Even after eight years only trace quantities of oil could be detected below the plow layer. There was no evidence that low molecular weight aromatic hydrocarbons were present in any soil layer after eight years exposure to oily sludges.

## 9.9 SURFACE WATER QUALITY

The water collected in the surface runoff ponds indicated that no serious contamination had occurred with either salts or organic compounds. At Lloydminster, where water was monitored for 8 years, the run-off pond was initially contaminated with chlorides, nitrate, and sulphate but concentrations decreased steadily thereafter, and were within Canadian Drinking Water Standards when last sampled.

## 9.10 GROUNDWATER QUALITY

Groundwater at some sites became contaminated with chlorides and nitrates, and at times exceeded Canadian Drinking Water Standards. Some of this contamination appeared to be due to leakages around the well casing, rather than leaching through the unsaturated zone.

The demonstration plots at Lloydminster were underlain by relatively low permeability silty to sandy clay till to a depth of at least 9 m. Fractures were detected in the till to a depth of approximately 2.5 m. Hydraulic conductivity values at the site varied from $10^{-5}$ cm $sec^{-1}$ to less than $10^{-6}$ cm $sec^{-1}$. The predominant direction of groundwater flow was to the east-northeast and the depth to water table at the site averaged 2.5 m. Monitor response time to water table fluctuation varied considerably with monitor depth.

Shallow groundwater beneath and down-gradient from the plots was contaminated, primarily with inorganic constituents. Chemical analysis showed only slight decreases in most parameters tested during the sampling period (September 1986 - August 1988). The relatively stable contaminant levels are thought to be due to ongoing leaching of the unsaturated zone as well as due to the slow groundwater movement.

The contamination with inorganic constituents decreased rapidly with depth although the groundwater was of poor quality. This

was partially due to the surface treatments (oily sludge, fertilizer). Factors exceeding Canadian Drinking Water Standards at Lloydminster included sulphate, magnesium, lead, manganese, ammonium, T.H., and T.D.S. It is not likely the lead originated from sludge but rather from till surficial deposits.

At no site did there appear to be contamination of groundwater with organics as indicated by carbon analyses. At Lloydminster, hydrocarbon levels were detected at the minimum detection level (50 $\mu g\ L^{-1}$) 3 years after the last sludge application; levels well below that which would affect water quality. When resampled in 1989 no hydrocarbons were detected in the groundwater.

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# APPENDIX TABLES

Appendix Table 1. Groundwater chemistry Lloydminster - September 10, 1986. All values in mg $L^{-1}$ except pH, SAR, and E.C. (ds $m^{-1}$).

| Parameter | C.D.W.S. | Well Number | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | P 174 | W 175 | P 176 | W 177 | P 178 | W 179 | P 180 | W 181 | W old |
| pH | | 7.6 | 8.0 | 7.7 | 7.9 | 7.6 | 7.9 | 7.8 | 8.0 | 7.8 |
| E.C. | | 2.9 | 0.9 | 4.3 | 5.5 | 2.8 | 1.4 | 3.8 | 2.8 | 3.3 |
| S.A.R. | | 0.5 | 0.3 | 1.6 | 2.1 | 0.6 | 0.4 | 1.8 | 0.5 | 1.6 |
| T.H. | 500 | 2075 | 560 | 2925 | 3550 | 1975 | 855 | 2455 | 1990 | 1450 |
| Ca | N.E. | 504 | 135 | 569 | 420 | 457 | 179 | 551 | 467 | 314 |
| Mg | 150 | 198 | 53 | 364 | 607 | 201 | 98 | 261 | 199 | 161 |
| K | N.E. | 12 | 5 | 15 | 15 | 10 | 4 | 13 | 8 | 3 |
| Na | 500 | 55 | 18 | 202 | 296 | 64 | 32 | 204 | 57 | 142 |
| $NH_4$-N | 0.5 | 1.1 | 0.0 | 1.4 | 0.2 | 2.3 | 0.0 | 0.8 | 0.3 | 0.1 |
| $NO_3$-N + $NO_2$-N | 10 | 0.0 | 3.3 | 0.1 | 6.6 | 0.07 | 2.87 | 0.0 | 7.0 | 11.6 |
| Cl | 250 | 4 | 3 | 8 | 12 | 2 | 257 | 11 | 4 | 815 |
| $SO_4$ | 500 | 1584 | 96 | 2735 | 3647 | 1560 | 196 | 2183 | 1584 | 141 |
| $HCO_3$ | N.E. | 601 | 568 | 534 | 580 | 571 | 416 | 636 | 461 | 460 |
| T.A. | 500 | 493 | 466 | 438 | 476 | 468 | 342 | 522 | 378 | 377 |
| T.D.S. | 1000 | 2655 | 607 | 4162 | 476 | 2580 | 987 | 3541 | 2580 | 1857 |
| C.O.D. | | 160 | 15 | 116 | 144 | 29 | 87 | 128 | 49 | 221 |
| Fe | 0.3 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.2 |
| Mn | 0.1 | 1.6 | 0.0 | 2.9 | 0.0 | 0.2 | 0.0 | 0.1 | 0.0 | 0.7 |
| Cu | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Zn | 5.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Pb | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

Appendix Table 2. Groundwater chemistry Lloydminster - December 10, 1986. All values in mg $L^{-1}$ except pH, SAR, and E.C. (ds $m^{-1}$).

| | C.D.W.S. | Well Number | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | P 174 | W 175 | P 176 | W 177 | P 178 | W 179 | P 180 | W 181 | W old |
| pH | | 7.0 | 7.5 | 7.0 | 7.4 | 7.0 | 7.4 | 7.1 | 7.5 | 7.5 |
| E.C. | | 2.9 | 0.9 | 4.3 | 5.6 | 2.8 | 1.8 | 3.9 | 3.0 | 3.2 |
| S.A.R. | | 0.6 | 0.3 | 1.7 | 2.2 | 0.7 | 0.6 | 1.8 | 0.6 | 1.4 |
| T.H. | 500 | 2000 | 550 | 2780 | 3770 | 1925 | 940 | 2400 | 2050 | 1360 |
| Ca | N.E. | 497 | 131 | 542 | 516 | 440 | 204 | 542 | 471 | 275 |
| Mg | 150 | 183 | 53 | 346 | 602 | 200 | 104 | 253 | 212 | 164 |
| K | N.E. | 12 | 6 | 16 | 14 | 10 | 4 | 14 | 7 | 4 |
| Na | 500 | 59 | 18 | 202 | 310 | 66 | 39 | 209 | 59 | 119 |
| $NH_4$-N | 0.5 | 1.7 | 0.0 | 2.8 | 0.2 | 1.1 | 0.0 | 3.4 | 0.1 | 0.1 |
| $NO_3$-N + $NO_2$-N | 10 | 0.0 | 2.8 | 0.0 | 5.0 | 0.0 | 5.1 | 0.0 | 4.7 | 14.7 |
| Cl | 250 | 2 | 3 | 8 | 10 | 3 | 230 | 11 | 4 | 744 |
| $SO_4$ | 500 | 1536 | 108 | 2735 | 3743 | 1536 | 302 | 2255 | 1704 | 134 |
| $HCO_3$ | N.E. | 640 | 566 | 517 | 629 | 576 | 447 | 644 | 497 | 466 |
| T.A. | 500 | 525 | 464 | 424 | 516 | 472 | 366 | 528 | 408 | 382 |
| T.D.S. | 1000 | 2610 | 612 | 4110 | 5530 | 2540 | 1130 | 3610 | 2730 | 1740 |

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

Appendix Table 3. Groundwater chemistry Lloydminster - January 6, 1987. All values in mg $L^{-1}$ except pH, SAR, and E.C. (ds $m^{-1}$).

| | C.D.W.S. | Well Number | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | W old | P 174 | W 175 | P 176 | W 177 | P 178 | W 179 | P 180 | W 181 | P 493 | P 494 | P 495 | P 496 | P 497 | P 498 | P 499 | P 500 | P 501 | P 502 | P 503 |
| pH | | 7.5 | 7.0 | 6.9 | 7.1 | 7.4 | 7.3 | 7.3 | 7.6 | 7.6 | 7.6 | 7.7 | 7.8 | 7.5 | 7.9 | 8.0 | 8.2 | 8.1 | 7.9 | 7.6 | 7.8 |
| E.C. | | 2.3 | 2.7 | 1.4 | 4.6 | 5.3 | 1.9 | 2.0 | 3.6 | 3.1 | 1.6 | 3.0 | 1.8 | 4.8 | 6.4 | 1.1 | 0.6 | 2.1 | 4.0 | 3.0 | 0.9 |
| S.A.R. | | 1.0 | 0.6 | 0.3 | 1.6 | 2.2 | 0.0 | 1.0 | 1.8 | 0.8 | 1.0 | 0.8 | 0.7 | 2.8 | 2.9 | 0.4 | 0.4 | 1.1 | 1.3 | 0.6 | 0.6 |
| T.H. | 500 | 1100 | 1975 | 940 | 2800 | 37225 | 2000 | 1125 | 2425 | 2350 | 925 | 2125 | 1075 | 3000 | 4500 | 700 | 345 | 1300 | 3000 | 2250 | 540 |
| Ca | N.E. | 220 | 479 | 251 | 540 | 497 | 469 | 250 | 550 | 530 | 210 | 510 | 230 | 500 | 559 | 179 | 74 | 250 | 500 | 540 | 136 |
| Mg | 150 | 133 | 188 | 75 | 352 | 602 | 200 | 121 | 255 | 249 | 97 | 206 | 121 | 425 | 753 | 60 | 38 | 164 | 425 | 218 | 48 |
| K | N.E. | 4 | 12 | 7 | 16 | 14 | 11 | 6 | 14 | 11 | 7 | 10 | 5 | 15 | 10 | 7 | 4 | 6 | 12 | 10 | 5 |
| Na | 500 | 73 | 57 | 23 | 200 | 303 | 69 | 52 | 204 | 89 | 66 | 85 | 55 | 358 | 450 | 23 | 18 | 92 | 163 | 69 | 29 |
| $NH_4$-N | 0.5 | 0.1 | 1.8 | 0.1 | 2.1 | 0.2 | 0.7 | 0.1 | 4.2 | 0.2 | 4.9 | 2.8 | 3.2 | 2.2 | 2.4 | 1.5 | 2.8 | 0.2 | 5.0 | 0.9 | 1.8 |
| $NO_3$-N + $NO_2$-N | 10 | 17.5 | 0.0 | 0.8 | 0.0 | 4.5 | 0.0 | 5.0 | 0.0 | 0.7 | 0.0 | 0.2 | 6.4 | 0.6 | 18.7 | 0.2 | 6.5 | 2.8 | 0.2 | 0.6 | 1.8 |
| Cl | 250 | 496 | 3 | 2 | 6 | 9 | 6 | 141 | 12 | 6 | 36 | 15 | 43 | 17 | 261 | 9 | 18 | 3 | 14 | 11 | 10 |
| $SO_4$ | 500 | 112 | 1478 | 475 | 2621 | 3599 | 1632 | 575 | 2279 | 2035 | 463 | 2006 | 806 | 3312 | 4492 | 400 | 40 | 825 | 2865 | 2102 | 288 |
| $HCO_3$ | N.E. | 505 | 643 | 593 | 565 | 63073 | 583 | 508 | 668 | 517 | 739 | 320 | 327 | 582 | 516 | 400 | 374 | 725 | 408 | 270 | 374 |
| T.A. | 500 | 414 | 527 | 486 | 463 | 517 | 478 | 417 | 550 | 424 | 606 | 262 | 268 | 314 | 423 | 328 | 307 | 594 | 334 | 222 | 306 |
| T.D.S. | 1000 | 1370 | 2540 | 1150 | 4020 | 5360 | 2680 | 1420 | 3640 | 3180 | 1250 | 3000 | 1460 | 4820 | 6870 | 881 | 412 | 1710 | 4190 | 3095 | 714 |

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

Appendix Table 4. Groundwater chemistry Lloydminster - April 14, 1987. All values in mg $L^{-1}$ except pH, SAR, and E.C. (ds $m^{-1}$).

| | C.D.W.S. | Well Number P 174 | W 175 | P 176 | W 177 | P 178 | W 179 | P 180 | W 181 | P 493 | P 494 | P 495 | P 496 | P 497 | P 498 | P 499 | P 500 | P 501 | P 502 | P 503 | W old |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | | 7.4 | 7.8 | 7.5 | 7.8 | 7.6 | 7.9 | 7.3 | 8.0 | 8.1 | 8.0 | 8.1 | 8.1 | 8.1 | 7.9 | 8.3 | 8.1 | 8.1 | 8.2 | 8.1 | 7.4 |
| E.C. | | 2.9 | 1.0 | 4.3 | 5.3 | 2.9 | 1.5 | 3.6 | 2.8 | 1.6 | 3.0 | 1.6 | 5.1 | 6.7 | 1.1 | 0.8 | 2.2 | 4.9 | 2.5 | 1.2 | 2.2 |
| S.A.R. | | 0.5 | 0.2 | 1.7 | 2.1 | 0.6 | 0.5 | 1.8 | 0 6 | 0.8 | 0.8 | 0.0 | 2.8 | 3.0 | 0.3 | 0.4 | 1.2 | 1.7 | 0.6 | 0.4 | 0.7 |
| T.H. | 500 | 1955 | 580 | 2775 | 3700 | 1890 | 790 | 2300 | 1900 | 900 | 1920 | 920 | 3075 | 4460 | 590 | 445 | 1275 | 3370 | 1575 | 670 | 1080 |
| Ca | N.E. | 469 | 130 | 485 | 479 | 412 | 158 | 504 | 400 | 195 | 438 | 174 | 450 | 467 | 147 | 90 | 218 | 518 | 359 | 153 | 198 |
| Mg | 150 | 189 | 62 | 379 | 607 | 208 | 94 | 252 | 218 | 99 | 200 | 118 | 473 | 799 | 54 | 52 | 177 | 504 | 164 | 69 | 140 |
| K | N.E. | 12 | 4 | 15 | 13 | 10 | 2 | 13 | 6 | 5 | 8 | 2 | 14 | 10 | 4 | 2 | 6 | 10 | 6 | 5 | 3 |
| Na | 500 | 55 | 13 | 209 | 299 | 64 | 32 | 193 | 62 | 55 | 75 | 43 | 358 | 455 | 18 | 18 | 96 | 232 | 52 | 25 | 55 |
| $NH_4$-N | 0.5 | 3.5 | 0.0 | 1.9 | 0.2 | 1.6 | 0.0 | 2.1 | 0.2 | 2.7 | 2.7 | 2.5 | 3.4 | 5.8 | 3.2 | 2.7 | 1.0 | 3.7 | 2.8 | 2.6 | 0.1 |
| $NO_3$-N + $NO_2$-N | 10 | 0.1 | 2.8 | 0.0 | 4.9 | 0.2 | 19.6 | 0.0 | 4.0 | 0.4 | 0.7 | 5.3 | 0.1 | 2.2 | 0.2 | 2.8 | 0.8 | 0.1 | 0.2 | 0.0 | 21.0 |
| Cl | 250 | 3 | 2 | 8 | 8 | 11 | 228 | 9 | 4 | 26 | 9 | 47 | 11 | 233 | 7 | 8 | 3 | 11 | 18 | 7 | 350 |
| $SO_4$ | 500 | 1463 | 108 | 2572 | 3638 | 1478 | 187 | 2087 | 1848 | 345 | 1632 | 586 | 3177 | 4271 | 168 | 40 | 825 | 3129 | 1190 | 283 | 153 |
| $HCO_3$ | N.E. | 637 | 599 | 572 | 607 | 562 | 389 | 622 | 518 | 740 | 462 | 401 | 530 | 674 | 563 | 540 | 734 | 605 | 515 | 515 | 538 |
| T.A. | 500 | 522 | 492 | 469 | 498 | 461 | 320 | 510 | 424 | 606 | 379 | 329 | 434 | 575 | 462 | 450 | 602 | 496 | 422 | 422 | 442 |
| T.D.S. | 1000 | 2510 | 629 | 3960 | 5370 | 2470 | 920 | 3370 | 2480 | 1100 | 2600 | 1190 | 4750 | 6600 | 681 | 501 | 1690 | 4700 | 2050 | 801 | 1260 |
| Fe | 0.3 | 0.1 | - | 0.2 | - | 0.5 | - | 0.7 | - | 1.0 | 0.3 | 0.1 | 0.5 | 0.1 | 0.3 | 1.2 | - | 0.8 | 0.3 | 0.8 | - |
| Mn | 0.1 | 1.8 | - | 4.3 | 0.2 | 1.4 | - | 2.3 | - | 2.6 | 3.0 | 0.3 | 7.0 | 4.0 | 2.1 | 1.7 | 0.1 | 7.1 | 1.7 | 2.2 | 0.2 |
| Cu | 1.0 | - | - | - | - | - | - | - | - | - | - | - | | - | - | - | - | - | - | - | - |
| Zn | 5.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Pb | | - | - | 0.1 | 0.1 | - | - | 0.1 | - | - | - | - | 0.1 | 0.1 | - | - | - | 0.1 | - | - | - |

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

Appendix Table 5. Groundwater chemistry Lloydminster - September 2, 1987. All values in mg $L^{-1}$ except pH, SAR, and E.C. (ds $m^{-1}$).

| Parameter | C.D.W.S. | Well Number | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | P 174 | W 175 | P 176 | W 177 | P 178 | W 179 | P 180 | W 181 | P 493 | P 494 | P 495 | P 496 | P 497 | P 498 | P 499 | P 500 | P 501 | P 502 | P 503 | Pond | W old |
| pH | | 7.5 | 7.9 | 7.5 | 7.8 | 7.7 | 7.9 | 7.8 | 7.4 | 7.8 | 7.6 | 7.6 | 7.3 | 7.3 | 8.0 | 7.7 | 7.3 | 7.4 | 7.4 | 7.6 | 6.8 | 7.2 |
| E.C. | | 2.8 | 1.0 | 4.4 | 5.5 | 3.1 | 1.8 | 3.9 | 2.0 | 1.7 | 2.8 | 1.7 | 1.3 | 5.5 | 0.7 | 6.5 | 2.4 | 5.1 | 2.4 | 1.4 | 0.6 | 3.3 |
| S.A.R. | | 0.5 | 0.3 | 1.7 | 2.2 | 0.7 | 0.5 | 1.8 | 0.5 | 0.9 | 0.7 | 0.6 | 0.3 | 2.9 | 0.3 | 2.7 | 1.2 | 2.2 | 0.6 | 0.5 | 1.8 | 1.6 |
| T.H. | 500 | 1836 | 560 | 2740 | 3450 | 2005 | 910 | 2310 | 1135 | 780 | 1750 | 955 | 705 | 3110 | 379 | 3930 | 1240 | 3080 | 1385 | 720 | 148 | 1455 |
| Ca | N.E. | 424 | 120 | 457 | 440 | 424 | 181 | 489 | 240 | 156 | 402 | 173 | 154 | 424 | 70 | 440 | 195 | 400 | 300 | 143 | 39 | 259 |
| Mg | 150 | 188 | 62 | 387 | 571 | 229 | 111 | 263 | 131 | 94 | 181 | 126 | 76 | 498 | 49 | 687 | 182 | 505 | 154 | 88 | 11 | 195 |
| K | N.E. | 11 | 3 | 14 | 12 | 10 | 3 | 12 | 4 | 4 | 7 | 1 | 4 | 13 | 2 | 8 | 6 | 11 | 5 | 5 | 3 | 4 |
| Na | 500 | 52 | 18 | 213 | 299 | 75 | 39 | 207 | 39 | 62 | 73 | 46 | 20 | 384 | 16 | 400 | 103 | 282 | 55 | 32 | 50 | 140 |
| $NH_4$-N | 0.5 | 2.7 | 0.1 | 2.1 | 0.2 | 1.7 | 0 | 2.5 | 0.1 | 9.8 | 4.0 | 0.9 | 2.8 | 2.8 | 2.5 | 3.9 | 3.6 | 2.4 | 4.4 | 2.0 | 0.1 | 0.3 |
| $NO_3$-N + $NO_2$-N | 10 | 0.1 | 3.0 | 0.3 | 4.6 | 0.0 | 3 | 0.1 | 3.8 | 0.4 | 0.4 | 5.4 | 0.2 | 1.3 | 1.7 | 12.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 8.8 |
| Cl | 250 | 4 | 2 | 7 | 9 | 2 | 227 | 10 | 3 | 101 | 14 | 54 | 3 | 34 | 5 | 307 | 3 | 10 | 26 | 6 | 82 | 588 |
| $SO_4$ | 500 | 1387 | 123 | 2706 | 3542 | 1665 | 276 | 2207 | 912 | 249 | 1439 | 575 | 229 | 3340 | 70 | 3580 | 883 | 3072 | 1075 | 335 | 77 | 476 |
| $HCO_3$ | N.E. | 639 | 571 | 568 | 602 | 574 | 439 | 608 | 335 | 676 | 479 | 426 | 649 | 552 | 427 | 596 | 740 | 687 | 479 | 583 | 78 | 489 |
| T.A. | 500 | 524 | 468 | 466 | 494 | 471 | 360 | 499 | 275 | 555 | 393 | 350 | 533 | 453 | 351 | 489 | 607 | 564 | 393 | 479 | 65 | 402 |
| T.D.S. | 1000 | 2387 | 626 | 4073 | 5192 | 2693 | 1061 | 3495 | 1513 | 1016 | 2361 | 1214 | 815 | 4976 | 436 | 5781 | 1744 | 4624 | 1858 | 901 | 305 | 1946 |
| C.O.D. | | 35 | 5 | 80 | 130 | 30 | 50 | 35 | 25 | 215 | 100 | 75 | 75 | 180 | 70 | 215 | 85 | 205 | 60 | 45 | 160 | 175 |
| T.O.C. | | 11 | 5 | 26 | 54 | 9 | 13 | 9 | 10 | 39 | 29 | 29 | - | 64 | 18 | 84 | 24 | 61 | 26 | 14 | 53 | 24 |
| Fe | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 | 0.7 | - | 0.3 | - | - | 0.3 | 0.3 | - | - | - | 1.6 | 0.2 | 0.2 | 0.1 | 0.4 | - | - |
| Mn | - | 1.9 | - | 4.0 | - | 1.5 | - | 2.2 | - | 1.6 | 1.9 | 0.3 | 2.2 | 5.0 | 0.6 | 1.6 | 0.2 | 4.7 | 0.9 | 2.4 | - | 0.2 |
| Cu | 1.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Zn | 5.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Pb | - | 0.1 | - | 0.1 | 0.1 | 0.1 | - | - | - | - | - | - | - | 0.1 | - | 0.1 | - | 0.1 | - | - | - | - |

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

Appendix Table 6. Groundwater chemistry Lloydminster December 1, 1987. All values in mg $L^{-1}$ except pH, SAR, and E.C. (ds $m^{-1}$).

| Parameter | C.D.W.S. | Well Number | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | W 331 | W 332 | P 174 | W 175 | P 176 | W 177 | P 178 | W 179 | P 180 | W 181 | P 494 | P 495 | P 496 | P 497 | P 498 | P 499 | P 500 | P 501 | P 502 | P 503 | P 493 | W old |
| pH | | 7.0 | 7.0 | 7.0 | 7.2 | 7.0 | 7.4 | 7.1 | 7.2 | 7.5 | 7.7 | 7.8 | 7.6 | 7.6 | 7.8 | 7.9 | 7.6 | 8.1 | - | 7.8 | 8.0 | 8.0 | 7.9 |
| E.C. | | 1.4 | 3.6 | 2.7 | 1.0 | 4.2 | 5.4 | 2.9 | 2.8 | 3.8 | 2.5 | 2.8 | 2.2 | 5.3 | 7.0 | 1.5 | 0.9 | 2.3 | - | 2.5 | 1.4 | 1.5 | 2.8 |
| S.A.R. | | 0.7 | 1.1 | 0.5 | 0.4 | 1.6 | 2.1 | 0.6 | 0.7 | 1.8 | 0.6 | 0.9 | 0.7 | 2.9 | 3.6 | 0.6 | 0.3 | 1.3 | - | 0.7 | 0.5 | 1.2 | 0.8 |
| T.H. | 500 | 705 | 2360 | 1805 | 580 | 2720 | 3580 | 1890 | 1725 | 2265 | 1605 | 1790 | 1350 | 3150 | 4280 | 700 | 520 | 1260 | - | 1590 | 755 | 750 | 1305 |
| Ca | N.E. | 144 | 491 | 424 | 119 | 497 | 416 | 408 | 385 | 450 | 340 | 408 | 255 | 393 | 404 | 124 | 91 | 190 | - | 336 | 159 | 132 | 226 |
| Mg | 150 | 83 | 274 | 181 | 68 | 358 | 617 | 211 | 184 | 277 | 182 | 187 | 172 | 526 | 794 | 94 | 71 | 189 | - | 182 | 86 | 101 | 179 |
| K | N.E. | 4 | 10 | 11 | 3 | 15 | 13 | 10 | 8 | 13 | 5 | 7 | 3 | 14 | 11 | 5 | 1 | 6 | - | 7 | 5 | 4 | 2 |
| Na | 500 | 48 | 128 | 52 | 23 | 202 | 301 | 66 | 69 | 204 | 55 | 92 | 62 | 384 | 552 | 36 | 18 | 112 | - | 64 | 32 | 75 | 69 |
| $NH_4$-N | 0.5 | 0.2 | 0.4 | 2.8 | 0.1 | 2.4 | 0.2 | 1.2 | 0.2 | 2.5 | 0.2 | 2.0 | 1.7 | 1.3 | 1.5 | 2.9 | 0.8 | 0.6 | - | 2.0 | 1.1 | 0.7 | 0.2 |
| $NO_3$-N + $NO_2$-N | 10 | 4.1 | 0.3 | 0.0 | 1.4 | 0.0 | 3.7 | 0.0 | 2.7 | 0.1 | 3.9 | 1.7 | 0.1 | 0.1 | 9.0 | 0.0 | 0.1 | 0.3 | - | 0.5 | 0.2 | 0.4 | 17.5 |
| Cl | 250 | 21 | 9 | 4 | 5 | 9 | 10 | 3 | 86 | 12 | 4 | 14 | 32 | 8 | 276 | 2 | 3 | 2 | - | 26 | 6 | 28 | 627 |
| $SO_4$ | 500 | 306 | 2155 | 1377 | 139 | 2673 | 3523 | 1478 | 1228 | 2068 | 1271 | 1507 | 954 | 3369 | 4118 | 383 | 73 | 902 | - | 1147 | 304 | 298 | 96 |
| $HCO_3$ | N.E. | 556 | 423 | 632 | 598 | 559 | 618 | 571 | 519 | 611 | 503 | 517 | 525 | 617 | 754 | 445 | 615 | 639 | - | 584 | 607 | 713 | 457 |
| T.A. | 500 | 456 | 347 | 519 | 490 | 459 | 507 | 469 | 426 | 501 | 413 | 424 | 431 | 506 | 618 | 365 | 505 | 524 | - | 479 | 498 | 585 | 375 |
| T.D.S. | 1000 | 901 | 3281 | 2367 | 659 | 4036 | 5204 | 2462 | 2231 | 3331 | 1126 | 2481 | 1739 | 5003 | 6571 | 870 | 565 | 1722 | - | 2056 | 895 | 996 | 1504 |
| C.O.D. | | 68 | 52 | 26 | 28 | 74 | 134 | 18 | 44 | 34 | 20 | 74 | 114 | 154 | 234 | 66 | 54 | 56 | 192 | 52 | 42 | 66 | 92 |
| T.O.C. | | 32 | 17 | 9 | 5 | 24 | 55 | 9 | 16 | 10 | 11 | 23 | 29 | 60 | 86 | 17 | 14 | 21 | 57 | 16 | 12 | 18 | 11 |
| Fe | 0.3 | 0.6 | 0.9 | 0.3 | - | - | - | 0.3 | - | - | - | - | 0.6 | 0.4 | 0.1 | 0.5 | - | - | 0.4 | - | 0.2 | - | - |
| Mn | - | 0.6 | 1.0 | 2.0 | 2.0 | 4.3 | - | 1.7 | - | 2.4 | - | 2.1 | 2.9 | 2.8 | 0.6 | 2.2 | 1.0 | 0.3 | 3.9 | 2.1 | 1.8 | 0.7 | - |
| Cu | 1.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Zn | 5.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Pb | - | 0.2 | 0.1 | - | - | 0.1 | 0.1 | 0.1 | - | 0.1 | - | - | - | 0.1 | 0.1 | - | - | - | 0.1 | - | 0.1 | - | - |

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

Appendix Table 7. Groundwater chemistry Lloydminster - July 15, 1988. All values in mg $L^{-1}$ except pH, SAR, and E.C. (ds $m^{-1}$).

| Parameter | C.D.W.S. | Well Number | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | P 174 | P 176 | P 178 | P 180 | P 493 | P 494 | P 495 | P 496 | P 497 | P 498 | P 499 | P 500 | P 501 | P 502 | P 503 | Pond | W 175 | W 177 | W 179 | W 181 | W old |
| pH | | 7.5 | 7.3 | 7.4 | 7.5 | 7.8 | 7.6 | 7.9 | 7.8 | 8.0 | 7.7 | 8.2 | 7.9 | 7.8 | 7.9 | 8.1 | 7.4 | 7.7 | 7.6 | 7.7 | 7.7 | 7.7 |
| E.C. | | 2.8 | 4.3 | 2.9 | 3.8 | 1.4 | 2.9 | 2.0 | 5.0 | 7.4 | 1.3 | 0.9 | 2.0 | 4.9 | 2.6 | 1.3 | 0.2 | 0.9 | 5.4 | 1.8 | 2.2 | 3.1 |
| S.A.R. | | 0.5 | 1.7 | 0.6 | 1.9 | 1.2 | 1.0 | 0.7 | 2.8 | 3.9 | 0.0 | 0.4 | 1.2 | 2.0 | 0.6 | 0.0 | 0.2 | 0.3 | 2.2 | 0.5 | 0.6 | 1.5 |
| T.H. | 500 | 1865 | 2810 | 1900 | 2280 | 675 | 1850 | 1145 | 3010 | 4360 | 790 | 510 | 1080 | 3130 | 1675 | 715 | 84 | 515 | 3690 | 905 | 1395 | 1340 |
| Ca | N.E. | 438 | 492 | 416 | 484 | 110 | 428 | 202 | 420 | 412 | 178 | 90 | 170 | 444 | 366 | 136 | 20 | 112 | 448 | 179 | 304 | 256 |
| Mg | 150 | 187 | 383 | 308 | 260 | 97 | 189 | 155 | 476 | 809 | 83 | 69 | 157 | 490 | 184 | 90 | 8 | 56 | 624 | 111 | 154 | 170 |
| K | N.E. | 12 | 14 | 10 | 12 | 5 | 8 | 2 | 12 | 10 | 5 | 2 | 6 | 9 | 7 | 5 | 5 | 4 | 12 | 3 | 6 | 3 |
| Na | 500 | 52 | 207 | 64 | 209 | 73 | 98 | 57 | 358 | 591 | 23 | 20 | 92 | 259 | 59 | 32 | 4 | 13 | 303 | 36 | 50 | 124 |
| $NH_4$-N | 0.5 | 1.7 | 1.5 | 0.5 | 1.5 | 0.2 | 1.1 | 0.2 | 0.9 | 0.5 | 0.5 | 0.2 | 0.2 | 1.1 | 1.0 | 0.5 | 0.2 | 0.1 | 0.2 | 0.2 | 0.2 | 0.2 |
| $NO_3$-N + $NO_2$-N | 10 | 0.0 | 0.0 | 0.1 | 0.3 | 4.3 | 2.1 | 6.3 | 0.2 | 21.7 | 0.5 | 5.7 | 2.1 | 1.1 | 0.4 | 0.2 | 0.0 | 2.0 | 3.8 | 1.1 | 5.3 | 8.7 |
| Cl | 250 | 3 | 6 | 5 | 1 | 9 | 12 | 91 | 0 | 332 | 2 | 4 | 4 | 77 | 30 | 5 | 19 | 3 | 9 | 270 | 5 | 709 |
| $SO_4$ | 500 | 1488 | 2641 | 1512 | 2127 | 220 | 1488 | 686 | 3102 | 4140 | 249 | 76 | 662 | 2833 | 1200 | 242 | 11 | 66 | 3515 | 203 | 950 | 185 |
| $HCO_3$ | N.E. | 616 | 576 | 563 | 618 | 745 | 532 | 466 | 560 | 782 | 688 | 542 | 689 | 649 | 585 | 634 | 80 | 571 | 626 | 461 | 547 | 453 |
| T.A. | 500 | 505 | 472 | 462 | 507 | 610 | 436 | 382 | 459 | 641 | 564 | 444 | 556 | 532 | 480 | 520 | 66 | 468 | 514 | 378 | 449 | 372 |
| T.D.S. | 1000 | 2490 | 4030 | 2500 | 3400 | 902 | 2500 | 1450 | 4650 | 6770 | 884 | 556 | 1440 | 4440 | 2140 | 827 | 109 | 547 | 5240 | 1040 | 1760 | 1710 |
| C.O.D. | | 30 | 68 | 26 | 27 | 34 | 66 | 72 | 113 | 224 | 35 | 21 | 41 | 117 | 51 | 26 | 35 | 9 | 137 | 98 | 52 | 237 |
| T.O.C. | | 9 | 22 | 8 | 8 | 12 | 22 | 22 | 58 | 78 | 11 | 9 | 15 | 51 | 13 | 9 | 12 | 9 | 53 | 13 | 10 | 43 |
| Fe | 0.3 | - | - | - | 3.9 | - | - | - | 0.1 | - | - | - | - | - | - | - | 0.3 | - | - | - | - | - |
| Mn | - | 1.9 | 4.0 | 1.6 | 2.7 | - | - | 0.1 | 1.8 | - | 0.7 | 0.2 | 0.1 | 1.8 | 1.4 | 0.6 | 0.1 | 0.1 | 0.1 | - | - | - |
| Cu | 1.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Zn | 5.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Pb | - | - | 0.1 | - | - | - | - | - | 0.1 | 0.1 | - | - | - | 0.1 | - | - | - | - | 0.1 | - | - | - |

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

Appendix table 8. Groundwater chemistry Lloydminster - August 8, 1989. All values in mg $L^{-1}$ except pH, SAR, and E.C. (ds $m^{-1}$).

| Parameter | C.D.W.S. | Well Number | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | P 174 | P 176 | P 178 | P 180 | P 495 | P 494 | P 495 | P 496 | P 497 | P 498 | P 499 | P 500 | P 501 | P 502 | P 503 | Pond | W 175 | W 177 | W 179 | W 181 | W 331 | W 332 | W old |
| pH | | 7.4 | 7.5 | 7.8 | 7.7 | 8.2 | 7.9 | 8.1 | 7.9 | 8.1 | 7.4 | 7.8 | 7.5 | 7.5 | 7.6 | 7.7 | 8.4 | 8.0 | 7.7 | 8.0 | 7.9 | 8.0 | 8.0 | 7.4 |
| E.C. | | 2.7 | 4.3 | 2.8 | 5.7 | 1.5 | 2.8 | 2.2 | 5.3 | 6.3 | 1.2 | 0.9 | 2.1 | 4.6 | 2.5 | 1.2 | 0.3 | 0.8 | 5.3 | 1.8 | 2.6 | 2.0 | 3.5 | 3.7 |
| S.A.R. | | 0.5 | 1.7 | 0.6 | 1.8 | 1.2 | 0.9 | 0.7 | 3.0 | 3.3 | 0.3 | 0.0 | 1.1 | 1.9 | 0.6 | 0.6 | 0.5 | 0.3 | 2.2 | 0.7 | 0.7 | 0.8 | 1.0 | 1.5 |
| T.H. | 500 | 1760 | 2750 | 1830 | 2220 | 758 | 1800 | 1280 | 3100 | 3770 | 710 | 520 | 1192 | 3020 | 1585 | 635 | 116 | 427 | 3490 | 920 | 1665 | 1005 | 2390 | 1625 |
| Ca | N.E. | 404 | 414 | 376 | 450 | 108 | 388 | 204 | 450 | 296 | 149 | 92 | 174 | 318 | 324 | 121 | 28 | 76 | 536 | 160 | 334 | 146 | 440 | 296 |
| Mg | 150 | 182 | 411 | 216 | 278 | 113 | 201 | 186 | 492 | 736 | 82 | 69 | 184 | 540 | 188 | 80 | 10 | 57 | 643 | 126 | 201 | 155 | 315 | 215 |
| K | N.E. | 10 | 15 | 9 | 12 | 3 | 7 | 1 | 12 | 8 | 4 | 2 | 5 | 9 | 5 | 4 | 7 | 2 | 11 | 3 | 5 | 3 | 8 | 3 |
| Na | 500 | 46 | 200 | 64 | 195 | 75 | 89 | 55 | 388 | 471 | 20 | 18 | 85 | 241 | 57 | 32 | 11 | 16 | 296 | 46 | 64 | 57 | 110 | 142 |
| $NH_4$-N | 0.5 | 0.8 | 0.9 | 0.1 | 0.8 | 0.1 | 0.2 | 0.1 | 0.4 | 0.2 | 0.2 | 0.0 | 0.1 | 0.5 | 0.2 | 0.1 | 0.2 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |
| $NO_3$-N + $NO_2$-N | 10 | 0.0 | 0.0 | 0.7 | 0.0 | 7.3 | 2.3 | 5.7 | 0.8 | 18.2 | 0.5 | 6.0 | 1.1 | 0.1 | 0.0 | 1.2 | 0.0 | 0.7 | 1.7 | 2.9 | 3.9 | 8.5 | 2.6 | 9.4 |
| Cl | 250 | 2 | 4 | 6 | 9 | 6 | 9 | 82 | 16 | 244 | 2 | 3 | 1 | 7 | 43 | 6 | 23 | 3 | 10 | 205 | 3 | 294 | 4 | 914 |
| $SO_4$ | 500 | 1287 | 2622 | 1469 | 2089 | 320 | 1488 | 850 | 3333 | 3650 | 206 | 157 | 782 | 2901 | 1147 | 243 | 32 | 52 | 3438 | 570 | 1301 | 233 | 2012 | 237 |
| $HCO_3$ | N.E. | 624 | 572 | 537 | 588 | 678 | 554 | 483 | 628 | 698 | 691 | 474 | 723 | 701 | 579 | 577 | 98 | 513 | 653 | 441 | 551 | 599 | 586 | 459 |
| T.A. | 500 | 512 | 470 | 440 | 482 | 556 | 454 | 396 | 515 | 572 | 566 | 388 | 592 | 574 | 475 | 473 | 86 | 421 | 536 | 362 | 452 | 492 | 480 | 376 |
| T.D.S. | 1000 | 2240 | 3950 | 2410 | 3500 | 992 | 2470 | 1640 | 4980 | 5850 | 808 | 604 | 1590 | 4360 | 2050 | 778 | 167 | 464 | 5060 | 1140 | 2200 | 1220 | 3190 | 2080 |
| C.O.D. | | 10 | 49 | 15 | 15 | 28 | 46 | 65 | 134 | 190 | 50 | 22 | 50 | 104 | 50 | 20 | 47 | 5 | 140 | 49 | 22 | 55 | 46 | 267 |
| T.O.C. | | 6 | 24 | 8 | 6 | 11 | 18 | 28 | 58 | 79 | 10 | 7 | 18 | 47 | 11 | 8 | 17 | 4 | 61 | 16 | 10 | 14 | 18 | 20 |
| Fe | 0.3 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Mn | - | 1.3 | 2.9 | - | 1.0 | - | 0.3 | - | 0.9 | - | 0.8 | - | - | 0.8 | 0.6 | - | - | - | - | - | - | - | 0.1 | - |
| Cu | 1.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Zn | 5.0 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Pb | - | - | 0.1 | - | - | - | - | - | 0.1 | 0.1 | - | - | - | 0.1 | - | - | - | - | 0.1 | - | - | - | - | - |

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards